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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1923.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society.*
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Child.	American Journal of Diseases of Children.
Amer. J. Hygiene	American Journal of Hygiene.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Anal. Fís. Quím.	Anales de la Sociedad Espanõla Física y Química.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industries à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. Report	Annual Reports of the Chemical Society.
Ann. Soc. géol. Belg.	Annales de la Société géologique de Belgique.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia Nazionale dei Lincei.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Brennstoff-Chem.	Brennstoff Chemie.
Brit. Assoc. Rep.	Report of the British Association for the Advancement of Science.
Brit. Med. J.	British Medical Journal.
Brit. Pat.	British Patent.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Asso. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. chim. Biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.

* The year is not inserted in references to 1923.

Abbreviated Title.	Journal.
Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
Chem. News	Chemical News.
Chem. Umschau	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
Chem. Weekblad	Chemisch Weekblad.
Chem. Ztg.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
D.R.-P.	Deutsches Reichs-Patent.
Econ. Geol.	Economic Geology.
Gazzetta	Gazzetta chimica italiana.
Geol. För. Förh.	Geologiska Föreningens i Stockholm Förhandlingar.
Helv. Chim. Acta	Helvetica Chimica Acta.
Internat. Mitt. Bodenkunde	Internationale Mitteilungen für Bodenkunde.
Japan. J. Phys.	Japanese Journal of Physics.
Japan. Pat.	Japanese Patent.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Bact.	Journal of Bacteriology.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan.
J. Chim. phys.	Journal de Chimie physique.
J. Exper. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Inst. Petr. Tech.	Journal of the Institution of Petroleum Technologists.
J. Landw.	Journal für Landwirtschaft.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Expt. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan.	Journal of the Pharmaceutical Society of Japan.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. S. African Chem. Inst.	Journal of the South African Chemical Institute.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Koll. Chem. Beihefte	Kolloidchemische Beihefte.
Kolloid Z.	Kolloid-Zeitschrift.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die Landwirtschaftlichen Versuchs-Stationen.
Lunds Univ. Årsskr.	Lunds Universitets Års-skrift.
Medd. om Grönland	Meddelser om Grönland.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.

Abbreviated Title.	Journal.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres	Mémorial des Poudres.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Naturwiss	Die Naturwissenschaften.
P.	Proceedings of the Chemical Society.
Pflüger's Archiv.	Archiv für die gesamte Physiologie des Menschen und der Thiere.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society of Experimental Biology and Medicine.
Quart. J. Med.	Quarterly Journal of Medicine.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. R. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften Wien.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Soil Sci.	Soil Science.
Stas. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
Swiss Pat.	Swiss Patent.
T.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
U.S. Pat.	United States Patent.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
Z. Krist.	Zeitschrift für Kristallographie.
Z. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Z. Nahr.-Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zentr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde, und Infektionskrankheiten.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

In the following report, the author has followed the customary practice of dealing with a limited number of selected topics.

Radiation and Ionisation Potentials.

The effects produced by the electronic bombardment of gas molecules have in late years occupied the attention of many workers who have sought, first, to determine the minimum electron energies or the critical potentials which are required to produce certain changes in the properties of the molecules or their constituent atoms, and, secondly, to ascertain the precise nature of these changes by reference to spectral and other observations. Not infrequently, the discrepancies between the experimental results obtained by different workers are such as to render any attempt at theoretical interpretation of doubtful value, and even although the recent literature affords evidence that a considerable advance has been made in the experimental technique, it seems doubtful whether the methods of investigation have yet been sufficiently developed to warrant the results being accepted with entire confidence.

On account of the structural simplicity of the atoms of hydrogen and helium, the critical potentials of these elements are of outstanding importance, and for this reason a brief account of some of the recent work on these gases will be given here.

Earlier work was summarised in the Annual Report for 1920.[1] It was there pointed out that the results obtained with hydrogen appeared to have established the existence of four critical potentials at 10·3, 13·9, 16·8, and 30·4 volts. Since then, the work of American investigators would seem to assign to hydrogen six critical potentials. Three of these at 10·1, 12·1, and 13·8 volts are, according to K. T. Compton,[2] atomic potentials, the first two being resonance potentials

[1] P. 13. [2] *Proc. Amer. Phil. Soc.*, 1922, **61**, 212; *A.*, ii, 350.

and the third representing the energy necessary to ionise the hydrogen atom. The three remaining critical voltages at 11·3, 12·8, and 16·2 volts are supposed to correspond respectively with the ionisation of the molecule, with the dissociation of the molecule plus excitation of the resulting hydrogen atom, and with the dissociation of the molecule plus ionisation of the atom.

The numbers obtained by P. S. Olmstead [3] are in remarkably good agreement with the figures which have been cited.

In continuation of previous work [4] on the subject, F. Horton and Miss A. C. Davies have found [5] that the behaviour of hydrogen is characterised by eight critical voltages, at which the changes summarised in the following table are said to occur. In this table the electron is represented by $\odot$, the ionised forms of the atom and molecule by $H^{\cdot}$ and $H_2^{\cdot}$, and radiating forms of the atom or molecule by the corresponding symbol enclosed in brackets.

Critical voltage.	Nature of the change produced.
10·2	Atomic excitation $H \longrightarrow (H)$.
11·9	Molecular excitation $H_2 \longrightarrow (H_2)$.
12·6	Dissociation and atomic excitation $H_2 \longrightarrow H + (H)$.
13·5	Atomic ionisation $H \longrightarrow H^{\cdot} + \odot$.
15·9	Dissociation and ionisation of one atom $H_2 \longrightarrow H + H^{\cdot} + \odot$.
22·8	Molecular ionisation $H_2 \longrightarrow H_2^{\cdot} + \odot$.
26·1	Dissociation plus atomic ionisation plus atomic excitation $H_2 \longrightarrow H^{\cdot} + (H) + \odot$.
29·4	Dissociation and ionisation of both atoms $H_2 \longrightarrow 2H^{\cdot} + 2\odot$.

The spectral observations made in connexion with the above measurements are for the most part in agreement with those recorded by O. S. Duffenback,[6] but in addition Horton and Davies have found that hydrogen gives rise to a continuous spectrum which is attributed to the formation of molecules from neutral atoms.

For the dissociation potential, which has no place in the above table, A. R. Olson and G. Glockler [7] have found 3·16 volts, and these authors claim to have detected breaks (corrected for the dissociation voltage) in the voltage current curves at 11·98, 12·68, 12·98, 13·14, and 13·24 volts which are in close agreement with the values calculated from the frequencies of five members of the Lyman series. If these measurements have any real significance, it would seem that the sensitiveness of the apparatus employed

[3] *Physical Rev.*, 1922, **20**, 613; *A.*, ii, 367.
[4] *Proc. Roy. Soc.*, 1920, [*A*], **97**, 23; *A.*, 1920, ii, 215.
[5] *Phil. Mag.*, 1923, [vi], **46**, 872; *A.*, ii, 820.
[6] *Physical Rev.*, 1922, **20**, 655.
[7] *Proc. Nat. Acad. Sci.*, 1923, **9**, 122; *A.*, ii, 455.

marks a very noteworthy advance in the experimental determination of characteristic potentials.

Turning to helium, reference may be made to the recent discovery [8] of hitherto unobserved lines in the ultra-violet spectrum which lead to a value of 24·5 volts for the ionisation potential. This is less than the value of 25·3 volts obtained previously in concordant series of measurements.[9] Further investigation [10] has shown, however, that the deviation is probably due to the fact that helium has two resonance potentials separated by only 0·8 volt at 19·7 and 20·5 volts, respectively. Since, in the earlier measurements, the primary excitation had been identified with the higher potential, it follows that the critical voltages previously assigned to helium and certain other gases require to be reduced by about 0·8 volt.[11]

This brief reference to recent literature suggests that the methods employed and the results obtained in the investigation of critical potentials are far less trustworthy than is commonly supposed. The interpretation given to the results is also by no means conclusive. Attention may be directed in this connexion to the criticism of J. S. Townsend,[12] who contends that the ionising potential does not, even approximately, afford a measure of the loss of energy of the ionising electron. The energy required to ionise an atom of helium is held to be about 12 volts, or about half the value usually accepted for the ionising potential. The procedure followed in the correlation of critical potentials with spectroscopic data has also been subjected to criticism.[13] Even in the simplest possible case—that of the monatomic molecule—it is argued that the true ionisation potential is much smaller than the value obtained by experiment.

The fact that the properties of a gas under certain conditions of excitation are so very markedly different from those of the gas in its normal state suggests that there may be a considerable accumulation of such excited or partly ionised molecules in the gaseous system when the conditions are favourable. In reference to this possibility, attention may be directed to the observations of J. Franck and P. Knipping [14] and of F. M. Kannenstine [15] on

[8] T. Lyman, *Nature*, 1922, **110**, 247; *A.*, 1922, ii, 674.

[9] J. Franck and P. Knipping, *Physikal. Z.*, 1919, **20**, 481; *A.*, 1920, ii, 72; F. Horton and (Miss) D. Bailey, *Phil. Mag.*, 1920, [vi], **40**, 440; *A.*, 1920, ii, 660.

[10] J. Franck, *Z. Physik*, 1922, **11**, 155; *A.*, 1922, ii, 811.

[11] Compare (Miss) A. C. Davies, *Phil. Mag.*, 1923, [vi], **45**, 786; A., ii, 281.

[12] *Phil. Mag.*, 1923, [vi], **45**, 1071; *A.*, ii, 366.

[13] W. M. Hicks, *ibid.*, p. 480; *A.*, ii, 209.

[14] *Loc. cit.*

[15] *Astrophys. Journ.*, 1922, **55**, 345.

metastable helium. From a study of the potential current curves which are obtained when helium is subjected to the action of intermittent unidirectional fields of varying periodicity, the latter has found that excited helium atoms can be detected for about 1/440th of a second after the removal of the exciting potential difference.

On the assumption that these excited atoms of low ionising potential are only produced by electronic impacts, it has been suggested that the above interval of time—an interval, it may be noted, which is very large in comparison with molecular periods—affords a measure of the time during which the excited condition persists in individual molecules. An average life period of this order of magnitude is at least 100,000 times as large as the values which have been previously obtained, and the interpretation given to the facts by Kannenstine is criticised by K. T. Compton,[16] who considers that the interval of time disclosed by the experiments has an entirely different significance. In Compton's view, the excited atoms are spontaneously transformed into normal atoms after a very much shorter average period, emitting in the process a quantum of resonance radiation which is absorbed and re-emitted by other atoms in the neighbourhood. In this way, resonance radiation is propagated throughout the gaseous system, the process having a formal similarity to those which are involved in problems of diffusion and a close analogy to the mechanism which has been suggested from time to time in explanation of certain types of chemical change. According to this interpretation of the facts, the interval of 1/440 second represents the time required for the dispersal of the resonance radiation, and in so far as it is possible to calculate the average life period of the excited helium atom on the basis of this view, a value is obtained which is not appreciably greater than the values derived for other substances by different methods.

The fact that hydrogen under widely varying conditions gives clearly defined critical voltages in close agreement with those calculated for the hydrogen atom suggests that hydrogen atoms have an average life period which is large compared with molecular time intervals. There is, however, a considerable difference between the recombination of neutral atoms to form molecules and the return of an excited atom to the normal condition, and this difference is quite in keeping with the results obtained by R. W. Wood,[17] which indicate that the average life period of a hydrogen atom is about 0·2 second. Such a period is long enough to account for the persistence of a considerable proportion of the atoms in gaseous

[16] *Phil. Mag.*, 1923, [vi], **45**, 750; *A.*, ii, 280.
[17] *Ibid.*, 1921, [vi], **42**, 729; *A.*, 1921, ii, 665.

hydrogen which is subjected to the dissociating influence of a force field.

Thermal Ionisation of the Elements.

Modern theories of atomic structure and radiation indicate that "enhanced" lines are probably due to ionised atoms, and M. N. Saha has shown [18] that certain characteristic features of the spectra of the solar prominences can be satisfactorily accounted for on the assumption that thermal ionisation is brought about under the combined influence of high temperature and low pressure. It would seem quite reasonable to suppose that those elements for which the intensity of the spark lines is relatively great are appreciably ionised in the high level solar chromosphere. By postulating a thermal equilibrium between atoms, ions, and electrons of the type

$$\mathrm{M} \rightleftharpoons \mathrm{M}^{\cdot} + \odot$$

and applying the usual thermodynamic considerations, we obtain

$$\log_e K = -\frac{Q_0}{RT} + \frac{\Delta C_p}{R} \log T + I/R \quad . \quad . \quad . \quad (1)$$

where K is the equilibrium constant, Q_0 is the limiting value of the heat of ionisation given by the equation $Q = Q_0 + T.\Delta C_p$, and I is the constant of integration.

The most novel feature in Saha's work consists in equating Q_0 with the energy of ionisation measured by NeV, where N represents the Avogadro number, e the unit electric charge, and V the ionisation potential. By the introduction of this value for Q_0 and by incorporating certain simplifying assumptions relative to the values of ΔC_p and I, which, if not exact, may at any rate be accepted as first approximations, equation (1) may be written in the form

$$\log_{10} K = -\frac{5048V}{T} + 2{\cdot}5 \log T - 6{\cdot}56 \quad . \quad . \quad . \quad (2)$$

in which $K = x^2p/1 - x^2$, where x denotes the degree of ionisation at pressure p.

It is thus possible to calculate the degree of thermal ionisation of any element under any given conditions of temperature and pressure if the ionisation potential of the element is known. The results of such calculations show that molecular hydrogen is completely dissociated into its component atoms in the solar atmosphere, but that the atoms of hydrogen and of helium are not appreciably ionised. On the other hand, it appears that the atoms of the

[18] *Phil. Mag.*, 1920, [vi], **40**, 472; *A.*, 1920, ii, 659.

alkaline-earth metals are nearly all ionised in the high level chromosphere, in which region the pressure is presumably very small, whereas at the lower levels the ionisation is only partial. The calculated results are in good agreement with spectroscopic observations.

The equation derived by Saha has recently been applied successfully to the interpretation of the results obtained by H. A. Wilson [19] in his experiments on the electrical conductance of flames containing salt vapours. These results were originally interpreted in terms of an empirical equation giving the connexion between the conductance and the concentration. It is now shown [20] that the measurements are consistent with the view that the conductivity of salts of the alkali metals in flames is due to electrons produced by thermal ionisation of the alkali metal atoms, the resulting positive ions having a negligible share in the conductance by reason of their small mobility.

At a fixed temperature, equation (2) leads to

$$\log K_2/K_1 = 5048(V_1 - V_2)/T$$

for the connexion between the ionisation constants and the corresponding ionisation voltages of the alkali metals, and by taking sodium ($V = 5{\cdot}11$ volts) as a standard of comparison, Noyes and Wilson have calculated from the flame conductivity data the ionisation potentials for the other alkali metals. The values so obtained are in fairly close agreement with those calculated [21] by application of the quantum theory from the frequencies of the characteristic spectral lines.

Discharge Spectra.

The changes produced in the discharge spectra of various substances by the admixture of helium or other inert gases have been studied in some detail. In the presence of helium there is a marked change in the relative intensities of the two hydrogen spectra in favour of the Balmer line series, although the applied potential is less than that corresponding with the resonance potential of the inert gas. When much helium is present, the secondary spectrum of hydrogen is no longer visible and the lines of shorter wavelength become relatively more intense. The results suggest [22] that the excited hydrogen molecules to which the secondary spectrum is attributed undergo dissociation as a result of collision with

[19] *Phil. Trans.*, 1915, [*A*], **216**, 63; *A.*, 1916, ii, 52.

[20] A. A. Noyes and H. A. Wilson, *J. Amer. Chem. Soc.*, 1922, **44**, 2806; *A.*, ii, 112.

[21] Hughes, *Nat. Research Council Bull.*, 1921, **2**, 168.

[22] V. von Kreussler, *Z. Physik*, 1923, **14**, 19; *A.*, ii, 446.

helium atoms and furnish thereby the hydrogen atoms required for the development of the Balmer lines.

Helium has also a very marked effect on the band and line spectra of carbon [23] which are developed in the passage of the discharge through vacuum tubes provided with carbon electrodes. With helium at a pressure of about 20 mm., it is possible to isolate very completely the "comet tail" bands by using a discharge tube provided with a palladium regulator and side tubes containing phosphoric oxide and potassium hydroxide. If under these conditions a condensed discharge is passed through the tube, an entirely new carbon spectrum is developed. It is suggested that the function of the helium is to facilitate the passage of the discharge whereby spectra characteristic of other gases at extremely low pressures are produced.

By the use of a discharge tube silvered on the inside it has been found [24] possible to obtain the secondary spectrum of hydrogen almost entirely free from the Balmer series of lines. The relative intensities of the secondary lines are changed very considerably when a spark gap is used in the discharge, the changes being very similar to those produced when the hydrogen is mixed with helium. The observations suggest that hydrogen only emits the Balmer line series when it is contaminated with other gases.

Several of the lines in the secondary hydrogen spectrum which have been found to be enhanced by helium are found [25] to be similarly intensified in the presence of argon, although the influence of the latter is much smaller than that of helium. Certain lines, previously observed only when helium was present in the discharge tube, are also developed when the hydrogen is mixed with argon.

Changes produced in the secondary spectrum of hydrogen by variations in the conditions of excitation have led to the suggestion [26] that lines of the spark type are due to ionised molecules, whilst those of the arc type are attributable to neutral molecules.

The method followed by Silberstein in deriving a formula for the line spectrum of neutral helium has been extended, with certain modifications, to the secondary spectrum of hydrogen.[27] Forty-seven lines are reproduced within one unit of frequency by the formula thus obtained. In reply to the criticism that the agreement between the calculated and observed frequencies in the case

[23] T. R. Merton and R. C. Johnson, *Proc. Roy. Soc.*, 1923, *A.*, **103**, 383; *A.*, ii, 446.

[24] E. Gehrcke and E. Lau, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1922, **32**, 453; *A.*, ii, 197.

[25] S. Barratt, *Phil. Mag.*, 1923, [vi], **46**, 627; *A.*, ii, 708.

[26] M. Kimura and G. Nakamura, *Japan. J. Phys.*, 1923, i, 85; *A.*, ii, 594.

[27] A. C. Menzies, *Nature*, 1922, **110**, 876; *A.*, ii, 45.

of helium is largely fortuitous, it is pointed out [28] that the probability that the coincidences are of this nature is less than $1{\cdot}7 \times 10^{-13}$.

The structure of the band spectrum of helium has been examined in detail [29] and the lines have been classified in accordance with Bohr's theory. The calculated moments of inertia of the helium atom in the stable and various metastable forms indicate that the displacement of an electron from the innermost to the next orbit has a much greater effect on the configuration of the atom than that which is produced by subsequent displacements in the transition from one metastable form to another. The classification of the helium bands referred to in this paragraph has been criticised [30] on the ground that combination relations are shown by the wave-lengths of lines which according to the scheme are supposed to belong to different groups.

In accordance with the view that the difference between the ions of the alkali metals and the atoms of the inert gases is confined to the nucleus, it has been found [31] that the frequencies of lines in the spark spectrum of potassium show relations which are very similar to those exhibited by the argon lines.

The passage of a discharge through the vapour given off by sodium amalgam produces a spectrum [32] in which the mercury lines show up very clearly if the temperature is below 100°. At higher temperatures, the mercury lines are almost entirely masked, and electric discharge under these conditions is recommended as a very convenient source of the *D*-lines. Since the relative intensities of the two spectra are probably determined by the ionising potentials of the two metals (Na 5·13, Hg 10·2 volts) and their partial pressures, it would seem that at low temperatures the atoms are so far apart that the electrons can acquire the energy necessary to ionise both the sodium and the mercury atoms. At higher temperatures, on account of the greater density of the vapour, the electrons attain less frequently the speed requisite for the ionisation of the mercury atoms, and the mercury lines disappear, although the proportion of this element in the mixed vapour is greater than at lower temperatures. This interpretation of the phenomena is supported by the observation [33] that the alkali metal spectrum obtained at 200° with uncondensed discharge is replaced by the

[28] L. Silberstein, *Nature*, 1923, **111**, 46; *A.*, ii, 46.

[29] W. E. Curtis, *Proc. Roy. Soc.*, 1922, *A*, **101**, 38; *A.*, 1922, ii, 330; *ibid.*, *A*, **103**, 315; *A.*, ii, 351.

[30] A. Kratzer, *Z. Physik*, 1923, **16**, 353; *A.*, ii, 595.

[31] P. Zeeman and H. W. J. Dik, *Ann. Physik*, 1923, [iv], **71**, 191; *A.*, ii, 670.

[32] F. H. Newman, *Phil. Mag.*, 1923, [vi], **45**, 181; *A.*, ii, 46.

[33] *Idem*, *ibid.*, p. 293; *A.*, ii, 103.

mercury spectrum when a condenser is introduced into the circuit.

Tesla-luminescence Spectra.

The spectrum emitted by benzene vapour rendered luminescent by the passage of a Tesla discharge [34] consists of a number of bands which are practically coincident with the stronger bands observed [35] in the absorption spectrum of the vapour. If the fluorescence spectrum given by alcoholic solutions of benzene is displaced towards the ultra-violet through a distance of 19 Å., whereby the influence of the solvent is eliminated, a close correspondence is found between the fluorescence bands and those of the Tesla spectrum. The agreement has been confirmed [36] by a recent investigation of the fluorescence spectrum of benzene vapour.

These results afford evidence of a close connexion between the Tesla-luminescence, the fluorescence, and the absorption spectra, and in their relations to one another these spectra recall the phenomena which are associated with the Frauenhofer effect.

Changes of temperature and pressure [37] have but little influence on the benzene spectrum, but the substitution of an atom of hydrogen produces changes [38] which differ widely according to the nature of the substituting atom or group. If this is linked to the benzene nucleus by an atom other than carbon, the benzene series of bands is either entirely obliterated or replaced by a faint continuous spectrum. Complete extinction results when hydrogen is replaced by the nitro-group, chlorine, or the CH_2Cl group. There is also no emission with *cyclo*hexane.

X-Ray Spectra.

As the results of a detailed comparison of the *X*-ray spectra of a large number of elements, N. Bohr and D. Coster [39] have been led to the conclusion that these exhibit no sign of the periodicity which is observable when the optical spectra are compared.

The values derived for the wave-length of homogeneous *X*-radiation by applying the formula $n\lambda = 2d \sin \theta$ to spectra of different orders are found [40] to exhibit deviations which cannot be explained by errors of experiment. The most satisfactory interpretation of the experimental data is afforded by Ewald's theory,[41] according

[34] W. H. McVicker, J. K. Marsh, and A. W. Stewart, *T.*, 1923, **123**, 642.
[35] W. N. Hartley, *Phil. Trans.*, 1908, *A*, **208**, 384.
[36] W. H. McVicker and J. K. Marsh, *T.*, 1923, **123**, 820.
[37] *Idem.*, *ibid.*, p. 817.
[38] W. H. McVicker, J. K. Marsh, and A. W. Stewart, *ibid.*, p. 2147.
[39] *Z. Physik*, 1923, **12**, 342; *A.*, ii, 110.
[40] E. Hjalmar, *ibid.*, 1923, **15**, 65; *A.*, ii, 448.
[41] *Ann. Physik*, 1917, [iv], **54**, 589.

to which the relation between the orders of the spectrum and the glancing angle is given by the equation log sin $\theta/n = A + B/n^2$, in which A and B are constants.

Ionisation of Electrolytes.

A critical examination of recent attempts to account for the behaviour of salt-like compounds in solution has led H. J. S. Sand to the conclusion [42] that complete ionisation is a necessary consequence of the postulation of a uniform dielectric medium. By the use of Boltzmann's probability theorem and of the law of ionic attraction indicated by the observations of Born and Landé, it is calculated that for a decinormal solution of a uni-univalent electrolyte in water, the probability that the ions are in close contact is 0·225 times the probability that the ions are separated by the maximum distance. On the assumption that there are no forces between the ions, the corresponding number is equal to 0·046, from which it follows that the effect of the electrical forces on the distribution of the ions of a salt such as sodium chloride in aqueous solution is very small. The smallness of the attraction effect may be more readily appreciated by comparing the above numbers with the value of the same probability ratio for the vapour of sodium chloride at 1000°. The value in question is $3{\cdot}4 \times 10^{16}$, from which it may be inferred that sodium chloride in the form of vapour will behave as an undissociated substance. Provided that the fundamental postulate is accepted, Sand's analysis would seem to justify the general correctness of the theories put forward by Sutherland, Milner, and Ghosh, and more recently by Bjerrum and by Debye.[43] It is pointed out,[44] however, that the assumption of a uniform dielectric medium would lead us to expect polarisation effects on the passage of a current through the solution, which would make the conductivity, when measured by the use of rapidly alternating currents and high potential gradients, appreciably greater than that found by the use of unidirectional currents and small potential gradients. Such differences have not been observed, and therefore it would appear that the idea of a uniform dielectric medium must be abandoned. In this connexion, attention may, however, be directed to the claim that variations in the conductivity of salt solutions have been observed [45] in experiments made with alternating current frequencies of the order of 10^6 per second.

In most theories of ionisation, comparatively little or no atten-

[42] *Phil. Mag.*, 1923, [vi], **45**, 129; *A.*, ii, 55.

[43] P. Debye and E. Hückel, *Physikal. Z.*, 1923, **24**, 185, 305; *A.*, ii, 459, 724.

[44] H. J. S. Sand, *Phil. Mag.*, 1923, [vi], **45**, 281; *A.*, ii, 120.

[45] M. Philippson, *Bull. Acad. roy. Belg.*, 1922, [v], **8**, 76; *A.*, ii, 212.

tion is given to the part played by the solvent. This point has been emphasised by J. Kendall and his co-workers, who in a long series of experimental studies have developed the view that, in ionisation equilibria, solvent and solute are essentially equivalent, and further have been led to the enunciation of a number of generalisations correlating the phenomena of compound formation, solubility, and ionisation.

This work has included the examination of various types of binary organic mixtures,[46] acid salts,[47] fused salts,[48] and aqueous solutions.[49] In all cases, the extent to which the components of the liquid mixtures combine to form compounds is found to depend primarily on the relative position of the constituent radicals in the electrochemical series. For example, in systems of the type HX — RX, compound formation increases regularly as the electrochemical difference between H and R increases. The solubilities of salts (RX) in acids (HX) are also dominated by the same factor, due consideration of which has made it possible to predict the solubility relations which are met with when more complex types of polar solutions are considered.[50] Electrical measurements indicate that ionisation runs parallel with compound formation.

On the basis of these and other results, a modified ionisation hypothesis has been advanced,[51] the principal feature of which is the idea that ionisation is a consequence of compound formation. In the additive compounds, the attractive forces between the radicals are diminished to such an extent that ionisation of the complex occurs quite readily, although the simple compound molecules may be quite stable. The behaviour of pure associated liquids can be readily interpreted in terms of the theory. Such exceptions as have been encountered in this work on solutions have been found to be due to the formation of substitution, as distinguished from addition, compounds.

Amphoteric Electrolytes.

In accordance with the views of Bredig, Walker, and Michaelis, it has been generally supposed that solutions of the amino-acids are

[46] *J. Amer. Chem. Soc.*, 1914, **36**, 1222, 1722, 2498; *A.*, 1914, i, 858, 1069; 1915, i, 15; *ibid.*, 1915, **37**, 149; *A.*, 1915, i, 80; *ibid.*, 1916, **38**, 1309, 1712; *A.*, 1916, i, 599, 707; *ibid.*, 1921, **43**, 1426; *A.*, 1922, ii, 33.

[47] *Ibid.*, 1920, **42**, 2131; 1921, **43**, 979, 1470, 1846; *A.*, 1921, ii, 45, 453; 1922, i, 5; 1922, ii, 126.

[48] *Ibid.*, 1923, **45**, 963; *A.*, ii, 387.

[49] *Ibid.*, 1917, **39**, 2303; *A.*, 1918, ii, 36.

[50] *Ibid.*, 1921, **43**, 1481, 1545; *A.*, 1922, ii, 34.

[51] *Ibid.*, 1917, **39**, 2323; 1921, **43**, 1416; 1922, **44**, 735; *A.*, 1918, ii, 37; 1922, ii, 32, 419; *Proc. Nat. Acad. Sci.*, 1921, **7**, 56; *A.*, 1921, ii, 491.

characterised by the presence of unchanged molecules $NH_2 \cdot R \cdot CO_2H$ and the ions $\overset{+}{N}H_3 \cdot R \cdot CO_2H$ and $NH_2 \cdot R \cdot \overset{-}{C}O_2$, the relative concentrations of the three entities being determined by the magnitudes of the basic and acid ionisation constants k_b and k_a. The smallness of the values of k_b and k_a has made it appear improbable that the doublet ion $\overset{+}{N}H_3 \cdot R \cdot \overset{-}{C}O_2$ can be present in measurable concentration.

Certain reactions which the amino-acids undergo cannot, however, be satisfactorily interpreted in terms of this theory, which, moreover, leads to values for k_b and k_a which are incompatible with the structural relations of the amino-acids. These discrepancies have been discussed by N. Bjerrum,[52] who contends that the neutral molecules present in solutions of the aliphatic amino-acids consist almost exclusively of doublet ions, from which the positive and negative ions are produced by hydrolysis in accordance with the reversible equations

$$\overset{+}{N}H_3 \cdot R \cdot \overset{-}{C}O_2 + \overset{+}{H} \rightleftarrows \overset{+}{N}H_3 \cdot R \cdot CO_2H \quad . \quad . \quad . \quad . \quad (1)$$

$$\overset{+}{N}H_3 \cdot R \cdot \overset{-}{C}O_2 + \overset{-}{O}H \rightleftarrows NH_2 \cdot R \cdot \overset{-}{C}O_2 + H_2O \quad . \quad . \quad (2)$$

The constants determining the equilibrium condition are derived in the usual way by application of the mass law. From (1) and (2), respectively, we obtain

$$K_A = [\overset{+-}{A}][\overset{+}{H}]/[\overset{+}{A}] \quad \text{and} \quad K_B = [\overset{+-}{A}][\overset{-}{O}H]/[\overset{-}{A}]$$

where $[\overset{+}{A}]$, $[\overset{-}{A}]$, and $[\overset{+-}{A}]$ denote the concentrations of the positive, negative, and doublet ions, respectively.

It is shown that K_A and K_B are connected with the constants k_b and k_a of the older theory by the equations

$$K_A = k_w/k_b \quad \text{and} \quad K_B = k_w/k_a,$$

where k_w is the ionic product for water.

According to Bjerrum's theory, it is apparent that the constant k_b, which was previously supposed to have reference to the basic group, is actually a quantity which is determined by the acidity of the carboxyl group. Similarly, k_a is dependent on the strength of the basic radical of the amino-acid.

Whilst the electrically neutral constituents formed by dissolving aliphatic amino-acids in water consist almost entirely of doublet ions, the properties of the aromatic amino-acids indicate that these solutions contain both non-ionised molecules and doublet ions, the relative proportions being determined by the values of K_A and

[52] *Z. physikal. Chem.*, 1923, **104**, 147; *A.*, i, 444.

K_B. On the other hand, solutions of the aminophenols contain such a small proportion of doublet ions that their behaviour can be satisfactorily interpreted in terms of the older theory.

Conduction of Electrolytes.

If fused salts or amalgams are brought into contact with soda-lime glass and a current is passed through the boundary surface, the sodium ions in the glass can be replaced to some extent by other metallic ions. Although such replacement frequently leads to disintegration, it has been possible to study the effect in some detail by the use of silver salts. In these circumstances, the mobility of the sodium-ions is indicated by the movement of the surface of separation in the direction of the positive current. By combining these observations with measurements of the quantity of electricity and of the change in weight of the glass resulting from the ionic replacement, it is calculated [53] that about 80 per cent. of the sodium in the glass takes part in the conduction. The percentage increases from 74·4 at 278° to 81·0 at 343°.

Transport and conductivity measurements [54] made on solutions containing the chlorides of sodium and potassium in varying proportions have given results which appear to be difficult to interpret in terms of theories which postulate that salts of this type are completely ionised. These results confirm previous data [55] in showing that the proportion of the positive current carried by the sodium-ion decreases with increasing dilution. They appear to show, further, that in a solution which contains 0·02 mol. of the mixed chlorides (in the ratio 3KCl : 1NaCl) per litre, the sodium-ion takes no part in the electrolytic transport of the current. Although ionic hydration may be partly responsible for the differences between the observed and calculated transport ratios, the authors consider that a complete explanation necessitates the assumption that complex ions such as $NaCl_2'$ and KCl_2' are formed.

Electrode Potentials.

An attempt [56] to measure the absolute value of the single electrode potential has been made by a new method. It is based on the assumption that an electric field will have no effect on a light

[53] C. A. Kraus and E. H. Darby, *J. Amer. Chem. Soc.*, 1922, **44**, 2783; *A.*, ii, 113.

[54] R. F. Schneider and S. A. Braley, *ibid.*, 1923, **45**, 1125; A., ii, 456. Compare S. A. Braley and J. L. Hall, *ibid.*, 1920, **42**, 1770; *A.*, 1920, ii, 662.

[55] G. M. Smith and T. R. Ball, *ibid.*, 1917, **39**, 179; *A.*, 1917, ii, 247; L. S. Wells and G. M. Smith, *ibid.*, 1920, **42**, 185; *A.*, 1920, ii, 361.

[56] A. Garrison, *ibid.*, 1923, **45**, 37; *A.*, ii, 115.

metallic needle, if this is suspended in a solution which contains the corresponding metal-ions in such concentration that there is no formation of an electrical double layer at the metal–liquid surface. By combining this zero potential electrode—a silver needle suspended in a solution of silver-ions—with a 0·1*N*-calomel electrode, it has been found that the absolute potential of the latter electrode lies between — 0·20 and — 0·10 volt at 25°. This is not very different from the value of — 0·13 volt obtained by Billitzer, and the agreement is considered to render nugatory the objections which have been urged against the method employed by the latter investigator.

The possibility of interpreting electrode potentials in terms of the change $M + OH' = MOH + \odot$ has been examined [57] in detail. The argument leads to the conclusion that electro-capillary methods of measuring absolute potentials afford results which are illusory.

Measurements [58] of the *E.M.F.*'s of cells of the types

$H_2Pt|HCl,HgCl|Hg$, Na amalgam$|NaCl,HgCl|Hg$, and

Na amalgam$|C_2H_5{\cdot}ONa|PtH_2$,

in which ethyl alcohol of minimum conductivity obtained by systematic purification was used as solvent, have given $1{\cdot}6 \times 10^{-11}$ for the ionised fraction at 25°. The value calculated from the observed minimal conductivity [59] is much greater, namely, $1{\cdot}0 \times 10^{-9}$. Since the electrometric method employed yields results which are reproducible within 0·0001 volt and avoids the necessity of estimating the magnitude of any boundary potential, it is believed that the potential method affords a substantially correct value for the ionised fraction. According to this value, ethyl alcohol is only ionised to about 1/100th of the extent to which water is ionised at the same temperature.

Refractive and Rotatory Dispersions.

The continued employment of arbitrary wave-length standards in the attempt to correlate the optical properties of organic compounds is rather difficult to understand in view of the circumstance that the importance of dispersion has been so frequently emphasised. The neglect of the dispersion factor is perhaps most noticeable in the continued use of formulæ such as those of Gladstone and Dale and of Lorenz and Lorentz in the comparative study of refractive power. Incidentally, it may be noted that in both these measures of refractive power the changes in the refractive index terms tend

[57] J. Heyrovský, *Proc. Roy. Soc.*, 1923, *A*, **102**, 628; *A.*, ii, 114.
[58] P. S. Danner, *J. Amer. Chem. Soc.*, 1922, **44**, 2832; *A.*, ii, 117.
[59] P. S. Danner and J. H. Hildebrand, *ibid.*, 1922, **44**, 2824; *A.*, ii, 116.

to be neutralised by the corresponding changes in density, and on this account variations in the molecular refractive power of organic compounds are largely dominated and obscured by the additivity of mass. This objection does not apply to the measure of the refractive power $R = Mn_D$ (molecular refraction coefficient) proposed by F. Eisenlohr and E. Wöhlisch,[60] but all formulæ which involve the use of light of a particular frequency are obviously unsatisfactory.

The neglect of the dispersion factor, as recently pointed out by R. H. Pickard and H. Hunter,[61] and in a further paper by Hunter,[62] is quite possibly responsible for the comparative failure of the older methods of procedure. So long as the substances compared have their dispersion controlled by absorption bands in the remote ultra-violet, the formulæ referred to yield results which afford some justification for the older methods employed in comparing the refractive powers. When, however, substances are used for which the dispersion controlling absorption band is much nearer to the visible region of the spectrum, the inadequacy of the older formulæ and of the methods employed becomes clearly evident.

From a consideration of the dispersion factor, it is not difficult to understand why it should be necessary to assign different values to the atomic refractive power of elements of variable valency such as nitrogen, sulphur, and phosphorus, to introduce special terms in order to take account of the effects produced by double and triple bonds and by ring closure, and to take account of the effects peculiar to conjugated systems of double bonds or of ketonic groups. All these factors tend to bring the controlling absorption band nearer to the visible spectral region, with the result that the effects of dispersion become more marked.

These disturbances due to dispersion suggest that the first step towards the solution of the problem of correlating the optical properties of organic compounds should be the determination of the functional relation $r = f(\lambda)$, where r represents the refractive power, the natural rotatory power, or the magnetic rotatory power, and λ the wave-length of the light concerned. Assuming that the equation $r = f(\lambda)$ is relatively simple, then the values of the characteristic constants in this equation should afford a basis for the comparison of the optical properties which is free from the objections which attach to the older methods of comparison.

In the two papers referred to above, it is suggested that suitable equations are furnished by the Sellmeier equation in the case of

[60] *Ber.*, 1920, **53**, [*B*], 1746; *A.*, 1920, ii, 717.
[61] *T.*, 1923, **123**, 434.
[62] *Ibid.*, p. 1671.

refractive dispersion, by the Drude equation [63] for natural rotatory dispersion, and a modified Drude equation for magnetic rotatory dispersion.

These may be written respectively

$$n^2 = a^2 + \Sigma\frac{b\lambda^2}{\lambda^2 - \lambda_0^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\alpha = \Sigma\frac{k}{\lambda^2 - \lambda_0^2}\ ^{64} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\delta = \frac{A}{\lambda^2} + \Sigma\frac{B}{\lambda^2 - \lambda_0^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

There is abundant evidence in support of formula (1) as a means of representing refractive dispersion. Formula (2) agrees very well with the optical rotation data obtained by Lowry and his co-workers,[65] and more recently the examination of some fifty dispersion curves by Rupe [66] has led to the conclusion that normal rotatory dispersion throughout the visible spectrum can be satisfactorily expressed by a single-term formula of the Drude type. The study of magnetic rotatory dispersion is in an undeveloped condition, but there is some evidence of the applicability of formula (3).

In the present state of the investigation of the three types of dispersion, chief interest centres in the fact that the values of the several dispersion constants represented by λ_0^2—the square of the wave-length of the dominant absorption band—are, for a given substance, identical within the limits of experimental error.

As a result of the examination of the nitrite of *d*-ethyl-*n*-hexylcarbinol (γ-nonyl nitrite), Pickard and Hunter [67] have indeed found that the rotation data lead to $\lambda_0 = 3680$ Å. and the refractive index measurements to $\lambda_0 = 3730$ Å., whilst photographic records of the absorption spectrum indicate that the dominant absorption band lies in the region $\lambda_0 = 3670$—3720 Å. Furthermore, Hunter has shown [68] that the refractive and the rotatory dispersion of *d-sec.*-octyl alcohol can be satisfactorily represented by simple (one term) Sellmeier and Drude equations, respectively, in both of which the dispersion constant λ_0^2 has the value 0·0283 when wave-lengths

[63] "The Theory of Optics," 1907.

[64] The earlier forms of rotatory dispersion equation can be derived as special cases from the Drude equation—compare R. H. Pickard and H. Hunter, *loc. cit.*

[65] Compare T. M. Lowry and T. W. Dickson, *T.*, 1913, **103**, 1067; 1915, **107**, 1173.

[66] H. Rupe and A. Akermann, *Annalen*, 1920, **420**, 1; *A.*, 1920, ii, 652.

[67] *Loc. cit.*, p. 441.

[68] *Loc. cit.*, p. 1678.

are expressed in microns. These facts not only provide support for the suitability of the dispersion equations (1) and (2), but also afford evidence in favour of the existence of some connexion between refractive index and rotatory power such as was sought on theoretical grounds by G. H. Livens.[69]

Although the natural rotatory dispersion of ethyl tartrate can only be expressed satisfactorily by a two-term equation of type (2), it has been suggested [70] that the magnetic rotatory dispersion conforms to the requirements of a one-term equation of the same type. As Hunter points out, there is, however, no agreement between the wave-lengths of the absorption bands which are predicted by these two equations, and this author is of the opinion that the magnetic rotatory dispersion is more suitably represented by the equation

$$\delta = \frac{A}{\lambda^2} + \frac{B}{\lambda^2 - 0{\cdot}03} + \frac{C}{\lambda^2 - 0{\cdot}056},$$

in which the dispersion constants have the same values as the constants in the two-term formula of the Drude type (2) which represents [71] the natural rotatory dispersion. This equation possesses the advantage that it contains a term which is independent of absorption bands and thus brings out the connexion between refraction and magnetic rotation. Such a connexion may be expected if it is assumed that the phenomenon of magnetic rotatory dispersion is due to the imposition of an element of asymmetry upon the paths of all the electrons which are effective in producing refractive dispersion. It is consistent with the fact that magnetic rotatory dispersion ratios are, in general, smaller than the corresponding natural rotatory dispersion ratios and also with the fact that there is no proportionality, as suggested by Wiedmann's "law," between the natural and the magnetic rotatory powers of optically active organic compounds.

The fact that the optically active secondary alcohols and ethers exhibit [72] simple rotatory dispersion under widely varying conditions, whilst the corresponding esters show complex dispersion at higher temperatures and in solution, has led to the suggestion that complex dispersion may be characteristic of substances which contain the carboxyl or an equivalent group.

It has been found, however, that, whereas the di-*d*-β-octyl esters [73]

[69] *Phil. Mag.*, 1913, [vi], **25**, 817; *A.*, 1913, ii, 543.
[70] T. M. Lowry, R. H. Pickard, and J. Kenyon, *T.*, 1914, **105**, 94.
[71] T. M. Lowry and J. O. Cutter, *T.*, 1922, **121**, 532.
[72] J. Kenyon and R. A. McNicol, *T.*, 1923, **123**, 14; H. Phillips, *ibid.*, p. 22.
[73] L. Hall, *T.*, 1923, **123**, 32.

of the saturated dicarboxylic acids containing from one to eleven methylene groups in the acid radical show in all cases complex rotatory dispersion, the di-*l*-menthyl esters [74] of the same series of acids exhibit dispersion which can be adequately represented by the simple (one term) Drude formula. Furthermore, the rotatory powers of the β-octyl esters vary considerably with change of temperature, whilst the menthyl esters are only slightly affected by such change. These facts seem to discredit the hypothesis that complex rotatory dispersion is an inherent property of the carboxyl group or its structural equivalents.

The data for the above two series of esters disclose a further interesting fact in that the β-octyl esters exhibit alternating high and low rotatory power, suggesting that this may be the consequence of alternating *cis-* and *trans*-structure of the saturated dicarboxylic acids and their derivatives. Since, however, the rotatory powers of the menthyl esters exhibit no such alternation, it would seem that variations in optical activity cannot be held to furnish evidence in support of the *cis-trans*-configuration hypothesis.

In accordance with a suggestion made by Frankland, the tetrahedral disposition of the carbon valencies may be expected, in favourable circumstances, to give to carbon chain compounds a spiral form, in which five carbon atoms would be required for each complete turn. If this view of the structural relations is accepted, it may be anticipated that when the physical properties of homologous compounds are compared, there will be irregularities or discontinuities exhibited at those points in the series at which the spiral has completed an integral number of complete turns. Generally speaking, the physical properties of such catenary series show no such irregularities, the only substantial evidence in favour of the spiral chain hypothesis being afforded by the rotatory powers of homologous series of optically active compounds. The literature dealing with such compounds has been examined [75] with results which appear to be favourable to the theory and to its extension to hetero-catenic compounds in which the chain of carbon atoms is interrupted by an atom of oxygen. Recent data [76] for the *n*-alkyl lactates are also regarded as affording evidence for the helical structure of the carbon chain.

Reaction Velocities.

According to the radiation theory, the velocity of a unimolecular reaction is given by the equation $\kappa = s \,.\, e^{-h\nu/kT}$, in which s on

[74] L. Hall, *T.*, 1923, **123**, 105.
[75] R. H. Pickard, J. Kenyon, and H. Hunter, T., 1923, **123**, 1.
[76] C. E. Wood, J. E. Such, and F. Scarf, *ibid.*, p. 600.

dimensional grounds represents a frequency. This frequency was identified by S. Dushmann [77] with the frequency of the active radiation, whereby the empirical formula $\kappa = \nu \cdot e^{-h\nu/kT}$ was obtained, which agrees fairly well with the observations on gaseous reactions. For this reason attempts have been made to provide the equation with a theoretical basis.

Equations of the required type have been derived by J. A. Christiansen,[78] A. C. McKeown,[79] and W. C. McC. Lewis.[80] The general conditions under which statistical formulæ may be transformed into the Dushman type of formula have also been considered by J. Rice.[81] More recently, Christiansen, in conjunction with H. A. Kramers,[82] has, however, drawn the conclusion that an adequate and satisfactory physical basis for the unimolecular equation can only be obtained when it is assumed that all chemical changes, whether of the first or of a higher order, are the result of molecular collisions. The equation derived by these authors, $\kappa = A \cdot e^{-Q/RT}$, is formally identical with the original Arrhenius formula. In this equation, $1/A$ represents, however, the average life of activated molecules of the reactant substance, such activated molecules being produced by collisions, and not by the absorption of radiant energy.

Attempts have been made to determine the approximate magnitude of the velocity coefficients of the reversible reactions $N_2O_4 \rightleftharpoons 2NO_2$ by measurements of the velocity of sound in the gas with waves of different lengths. If the time factor involved in the adjustment of the chemical equilibrium is of the same order as the vibration frequency, the velocity of sound through the gas should be found to vary with the pitch. Experiments made by H. Selle [83] have given a positive result leading to a value of $k = 440$ at 21° for the dissociation of N_2O_4. On the other hand, E. Grüneisen and E. Goens [84] obtained negative results with variations of pitch over a wide range and conclude that k must be greater than 10,000.

A novel method for the investigation of high-speed reactions has been described [85] and applied to the study of the rate of reduction of oxyhæmoglobin by sodium hyposulphite.

[77] *J. Amer. Chem. Soc.*, 1921, **43**, 397; *A.*, 1921, ii, 315.
[78] *Z. physikal. Chem.*, 1922, **103**, 91; *A.*, ii, 62.
[79] *Phil. Mag.*, 1923, [vi], **46**, 321; *A.*, ii, 623.
[80] *Ibid.*, p. 327; *A.*, ii, 623.
[81] *Ibid.*, p. 312; *A.*, ii, 622.
[82] *Z. physikal. Chem.*, 1923, **104**, 451; *A.*, 1924, ii, 28.
[83] *Ibid.*, p. 1; *A.*, ii, 297.
[84] *Ann. Physik*, 1923, [iv], **72**, 193; *A.*, ii, 741.
[85] H. Hartridge and F. J. W. Roughton, *Proc. Roy. Soc.*, 1923, *A*, **104**, 376; *A.*, ii, 746.

Explosive Reactions in Gases.

Recent observations on the phenomena attending the explosive combination of carbon monoxide with oxygen in the presence of other gases indicate that variations in the conditions of reaction exert a profound influence on the effects which are produced when foreign gases are present.

The experiments made by H. B. Dixon [86] on the speed of propagation of the detonation wave in carbon monoxide–knall gas mixtures, and the results obtained by W. Payman and R. V. Wheeler [87] in the investigation of the speed of the uniform movement of flame in mixtures of carbon monoxide and air, have shown that water vapour has an accelerating influence on the combustion which reaches a maximum when the gaseous mixture contains about 6 per cent. of water vapour.

On the other hand, the pressure–time records obtained [88] as a result of the explosive combustion of normal carbon monoxide–air mixtures at an initial pressure of 50 atmospheres afford evidence that small quantities of water vapour of the order of 0·05 per cent. reduce appreciably the time required for the attainment of the maximum explosion pressure, whereas larger quantities of water vapour are without measurable influence on the length of this time period.

A further difference between the high-pressure explosions and the flame experiments is shown by the fact that hydrogen appears to be more effective than steam in speeding up the reaction when this occurs under high-pressure conditions,[89] whereas observations [90] on the speed of the uniform movement indicate that water vapour is more effective than hydrogen in promoting the combustion of carbon monoxide in the flame.

In explanation of these apparent discrepancies, it has been suggested that certain factors come into play under the high-pressure conditions which are of no practical importance in the combustion of carbon monoxide at atmospheric pressure.

The figures below are derived from the pressure–time records obtained by W. A. Bone and his co-workers in explosion experiments with mixtures of the composition $2CO + O_2 + 4R$, where R represents O_2, CO, or N_2. The maximum pressure, corrected for cooling, is recorded under p, the time required for the development of maximum

[86] *Phil. Trans.*, 1893, **184**, 97.

[87] *T.*, 1923, **123**, 1251.

[88] W. A. Bone, D. M. Newitt, and D. T. A. Townend, *ibid.*, p. 2008.

[89] W. A. Bone and W. A. Haward, *Proc. Roy. Soc.*, 1921, *A*, **100**, 67; *A.*, 1921, ii, 628.

[90] W. Payman and R. V. Wheeler, *loc. cit.*

pressure under Δt, and the fall in pressure during the first second of time after the attainment of the maximum under Δp.

R.	p (atoms.).	Δt (sec.).	Δp (atmos.).
1. Oxygen	460	0·005	200
2. Carbon monoxide	455	0·01	197
3. Nitrogen	440	0·19	93

Since the heat capacities of the diluents in the three experiments are the same, the conclusion has been drawn [91] that the very considerable differences shown by the data for the nitrogen experiment, as compared with those for the experiments with oxygen and carbon monoxide, are due to the absorption of energy by the nitrogen molecules and the subsequent transformation of this absorbed internal energy into kinetic energy during the cooling of the reaction products and the admixed nitrogen. The comparatively slow rate of the chemical change in the explosion of normal mixtures of carbon monoxide and air at high pressures is therefore primarily attributable to the capacity of the nitrogen molecule to absorb the energy which is liberated in the combustion of carbon monoxide and not to any inherent slowness of the reaction. There is no evidence to show that this factor plays any significant part when carbon monoxide burns in air at the ordinary pressure. Its effects are only apparent when the molecules of the explosive mixture are in close proximity.

The above observations are of importance in directing attention to the circumstance that there may be considerable differences in the nature of high-speed gaseous reactions according to whether these reactions occur at low or high pressures. Such differences may be the cause of the apparent anomalies which have been referred to at the beginning of this section.

The disturbing influence of the nitrogen in the high-pressure explosion of carbon monoxide-air mixtures precludes the possibility of determining the effects which are produced by the admixture of small quantities of water vapour or hydrogen. Experiments in which the nitrogen was replaced by argon show, however, quite clearly that hydrogen has an accelerating influence under the conditions of the explosive reactions. This is in accord with recent observations on the speed of propagation of the explosive wave in mixtures containing carbon monoxide and hydrogen.[92]

Surface Films.

In his Presidential Address to the Chemistry Section at the 1923 meeting of the British Association, F. G. Donnan [93] gave an

[91] W. A. Bone, *Proc. Roy. Soc.*, 1923, *A*, **103**, 205.
[92] H. B. Dixon and N. S. Walls, *T.*, 1923, **123**, 1025.
[93] Compare *Chemistry and Industry*, 1923, **42**, 892.

interesting summary of the present state of our knowledge of the phenomena associated with matter segregated in boundary surfaces. Substantial evidence indicating the frequent occurrence of unimolecular layers of orientated molecules in such interfacial regions has now been obtained, and experiments made with aliphatic organic compounds show that the area appropriated by a single molecule is very nearly the same for all compounds belonging to this group, is independent of the nature of the interface, and corresponds with a diameter which is approximately equal to the distance between the atoms of carbon in the diamond.

Such films are characterised by a surface pressure, which has been measured by suitable methods. By the gradual addition of a substance such as oleic acid to a water surface, it is found [94] that the pressure increases to a limiting value, at which point the further addition of acid leads to the formation of a floating drop. This saturation surface pressure characterises the state of equilibrium between the substance in bulk and in the form of a two-dimensional surface layer.

Investigation of the influence of temperature on the films formed by fatty acids on the surface of water or of aqueous solutions has shown [95] that these films expand when the temperature reaches a certain value. The surface pressure exerted by these expanded films can be represented by an equation of the van der Waals type, in which "b" represents twice the area of the molecules and "v" the area of the surface layer.

Aromatic compounds [96] containing a polar group and a long chain in the para-position (for example, *p*-hexadecylphenol and *p*-hexadecylaniline) behave like the fatty acids, the phenol or amino-group forming the head of the orientated molecule in contact with water. The cross-sections of the head agree with the values derived for the cross-sections of the nuclei of aromatic compounds from *X*-ray measurements made with the corresponding crystalline forms.

The results obtained in a comprehensive study of the spreading of organic liquids on the surface of water or mercury, and of the spreading of water on organic liquids, afford considerable support for the view [97] that the phenomenon is determined by the positive or negative value of a quantity known as the spreading coefficient. This is defined by the equation

$$S_{AB} = W_{AB} - W_A \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[94] A. Marcelin, *Compt. rend.*, 1922, **175**, 346; *A.*, 1922, ii, 686.
[95] N. K. Adam, *Proc. Roy. Soc.*, 1922, *A*, **101**, 516; *A.*, 1922, ii, 687.
[96] *Idem*, *ibid.*, 1923, *A*, **103**, 676; *A.*, ii, 539.
[97] W. D. Harkins and A. Feldman, *J. Amer. Chem. Soc.*, 1922, **44**, 2665; *A.*, ii, 127.

in which S_{AB} is the coefficient relating to the spreading of a liquid, A, on the surface of B, W_{AB} is the energy of adhesion per unit area of the liquid interface, and W_A is the energy of cohesion of the spreading liquid.

Since W_{AB} corresponds with the work which must be done to separate A and B, it may be written in the form $W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}$, where γ_A and γ_B are the ordinary surface tensions of A and B and γ_{AB} is the tension characteristic of the liquid interface.

In the same way, $W_A = 2\gamma_A$ and by substitution in (1) the value of the spreading coefficient is given by

$$S_{AB} = \gamma_B - (\gamma_A + \gamma_{AB}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since the process of spreading involves the replacement of the surface of B by an equal area of the surface of A together with an equal area of the liquid interface AB, it follows that the spreading coefficient as defined by equation (1) is a measure of the diminution of the free energy of the system. According to Harkins and Feldman, the liquid A will spread on the surface of B if the coefficient has a positive value, that is to say, if the energy of adhesion at the liquid interface is greater than the cohesive energy of the spreading liquid. Since W_A and W_B may have very different values, it follows that the behaviour may be quite different when the two liquids are interchanged.

When the spreading coefficient has a relatively high value, the film formed by the spreading of organic liquids on water is of unimolecular thickness. It would seem that these high values are only obtained when the molecules of the spreading liquid contain a polar group. It may be that such polar groups are of fundamental importance when it is a question of the formation of unimolecular films, but films of greater thickness may apparently be produced in the absence of any recognisable polarity in the molecules of the spreading substance.

Since the adhesive forces between liquids and inorganic solids are large in comparison with the cohesive forces of the great majority of liquids, it is to be expected that liquids will, as a rule, spread on solid surfaces. In practice, it is often found that spreading does not occur, and in such cases it may be inferred that the surface of the solid is already covered with a film of some foreign substance. The function of soap solutions and other cleansing agents is to remove such films by the substitution of other films which may be more easily eliminated.

Colloids.

When hydrosols of gelatin, soaps, etc., are employed for the study of the reversible change sol $\rightleftarrows$ gel, the interpretation of

the observations tends to be unduly complicated by the disturbing influence of hydrolytic reactions. For this reason, simpler relations may be anticipated when the aqueous dispersive medium is replaced by a relatively inert organic solvent such as that employed by E. W. J. Mardles [98] in his observations on organosols prepared by dissolving cellulose acetate in benzyl alcohol. An additional advantage is that the behaviour of these organosols is not unduly obscured by those various circumstances which are implied in the use of the term " thermal history."

As a result of various types of physical measurements, it has been possible to recognise three stages in the process of gelation. These stages occur for the most part in the following sequence : (1) the coalescence of fine to larger particles, (2) the aggregation of these larger particles into clusters, (3) the linking of the clusters to form a rigid jelly structure. The time factor associated with these several changes in its dependence on the concentration and temperature of the organosol has been elucidated by measurements of the light-scattering power (Tyndall number), of the viscosity and density, and of the rigidity.

In agreement with the experience of Freundlich, Hatschek, and others, it has been found that trustworthy viscosity data for gelating sols can only be obtained when the experimental conditions are such that high rates of shear are avoided. For this reason, viscometers of the capillary tube type are unsuitable, and the use of the falling-sphere viscometer [99] is recommended.

Tyndall number and viscosity measurements indicate the existence of a maximum gelation temperature, above which the sol form is quite stable. Below this temperature, the viscosity changes with time in accordance with the equation $\eta - \eta_0 = a \,.\, e^{kt}$, in which η_0 is the original viscosity of the sol (when the previous thermal history has ceased to be of appreciable significance), η is the viscosity after time t, a is a constant which depends on the concentration of the sol, and k is a coefficient which measures the rate of gelation. The temperature at which $k = 0$ is the maximum gelation temperature previously referred to.

The study of the reverse change (solation) has shown the existence of a minimum solation temperature, defined as the lowest temperature at which the viscosity of the melted gel returns to the value characteristic of the sol without the application of any mechanical treatment. The two temperatures are not identical, the difference between them depending on the concentration. It is suggested that this temperature difference affords a suitable

[98] *Trans. Faraday Soc.*, 1923, **18**, 327, 353, 365.
[99] W. H. Gibson and (Miss) L. M. Jacobs, *T.*, 1920, **117**, 473.

measure of the hysteresis which is characteristic of such systems.

On comparing the viscosities of the cellulose ester sols in the preparation of which different solvents have been used, it is found [1] that the least viscous sols are the most stable.

The suggestion has been made [2] that the term sol should not be applied to any liquid system if deviations from Poiseuille's law are exhibited when the liquid is made to flow through a capillary tube, or if its viscosity is affected by mechanical treatment. The manifestation of ageing phenomena of any kind should debar a liquid from inclusion in the group of sols.

Stable metallic sols containing both positively and negatively charged particles have been obtained [3] by the decomposition of benzene–toluene solutions of nickel carbonyl in presence of a small quantity of caoutchouc. The sol is coagulated by the addition of liquids in which the protective colloid is insoluble.

Arsenic sulphide, platinum, and carbon alcosols are quickly coagulated when mixed with alcohol containing a small quantity of anthracene and exposed to diffused light. In explanation, it is suggested [4] that the anthracene molecule loses an electron under the influence of the light and that coagulation is due to the adsorption of the residual positive ions by the negatively charged colloids.

The coagulation of the gold in the coloured beads which are produced by fusion of borax with auric chloride has been quantitatively investigated [5] by an ultra-microscopic method. The theory of Smoluchowski, which has already been applied with success to the coagulation of hydrosols at the ordinary temperature, is also found to accord very well with the observed rate of disappearance of the gold particles at 1,000°.

In connexion with the constitution of soap solutions, a more direct proof has been given,[6] by means of transport determinations, that the mobility of the ionic micelle is much greater than the sum of the mobilities of the constituent single ions. The results agree with the data obtained by other methods and show further that the micellary ions contain but little of the neutral colloidal constituent of the solutions.

[1] E. W. J. Mardles, *J. Soc. Chem. Ind.*, 1923, **42**, 127, 207; *A.*, i, 443.

[2] H. G. B. de Jong, *Rec. trav. chim.*, 1923, **42**, 1; *A.*, ii, 132.

[3] E. Hatschek and P. C. L. Thorne, *Proc. Roy. Soc.*, 1923, *A*, **103**, 276; *A.*, ii, 390.

[4] N. P. Peskov, *Kolloid Z.*, 1923, **32**, 238; *A.*, ii, 390.

[5] A. Ehringhaus and R. Wintgen, *Z. physikal. Chem.*, 1923, **104**, 301; *A.*, ii, 390.

[6] J. W. McBain and R. C. Bowden, *T.*, 1923, **123**, 2417.

Solutions of the alkali metal urates [7] form jellies which resemble those derived from soaps and other electrolytic colloids. The jellies show the presence of doubly refracting particles and radial structures, although the corresponding sols afford no evidence of such refraction either under the influence of a magnetic field or when the liquid is examined in a streaming condition.

Electronic Theories of Valency.

In view of the very considerable amount of space which is occupied in the chemical journals of 1923 by speculative discussions bearing on the electronic interpretation of valency and of the nature of valency bonds, it would perhaps be inappropriate to close this Report without some reference to the subject. The papers [8] read at a recent "General Discussion" afford some idea of the divergent views which are held with regard to the interpretation of the structural relations of both inorganic and organic compounds in terms of the electronic configuration of the atoms. These papers have been ably summarised by E. K. Rideal.[9]

For obvious reasons it is unnecessary to refer here to the applications of the electron theory to organic compounds. The cleavage between inorganic and organic chemistry is a more suitable subject.

According to N. V. Sidgwick,[10] the apparent difference between the valency theory of the organic chemist and the hypotheses which are associated with the interpretation of the structural relations of inorganic compounds is in no wise fundamental, in that the theory of atomic structure elaborated by Bohr [11] affords a simple and satisfactory account of the facts. In the building up of the elementary atoms in accordance with Bohr's scheme, certain elements—chromium, iron, cobalt, nickel, palladium, osmium, iridium, and platinum—are characterised by the tendency to develop an outer ring of six, instead of four or eight, electrons. Such elements may therefore be expected to show a sixfold symmetry of structure in their compounds corresponding with the co-ordination number six, just as organic compounds exhibit fourfold symmetry in accordance with the value of four for the co-ordination number of carbon.

The factors influencing co-ordination are discussed in reference to the stability of electron shells by T. M. Lowry [12] and C. H. Spiers.[13]

[7] E. Keeser and H. Zocher, *Koll. Chem. Beihefte*, 1923, **17**, 189; *A.*, ii, 135.
[8] *Trans. Faraday Soc.*, 1923, **19**, 450, 483.
[9] *Ibid.*, p. 539.
[10] *T.*, 1923, **123**, 725.
[11] N. Bohr, "The Theory of Spectra and Atomic Constitution," 1923.
[12] *Chemistry and Industry*, 1923, **42**, 316, 412; *A.*, ii, 313, 402.
[13] *Ibid.*, p. 534; *A.*, ii, 481.

The former considers that there are two types of co-ordination—centric and cyclic—but this view is criticised by J. D. M. Smith,[14] who holds that all co-ordination compounds are of the centric type.

The view that hydrogen is particularly suitable as a standard of valency because it possesses only one valency bond, and is consequently incapable of serving as a link between other elements, has been subjected to criticism [15] on the ground that compounds are known which, according to crystallographic and chemical evidence, undoubtedly contain co-ordinated hydrogen.

Noteworthy contributions to the subject of valency have also been made by W. Nernst [16] and Sir J. J. Thomson.[17]

H. M. Dawson.

[14] *Chemistry and Industry*, 1923, **42**, 847; *A.*, ii, 681.
[15] T. M. Lowry and H. Burgess, *T.*, 1923, **123**, 2111.
[16] *Z. angew. Chem.*, 1923, **36**, 453; *A.*, ii, 680.
[17] *Phil. Mag.*, 1923, [vi], **46**, 497; *A.*, ii, 682.

INORGANIC CHEMISTRY.

The output of work in inorganic chemistry has been well maintained in 1923, and the prefatory remarks of the Report for 1922 apply to that now submitted. As will appear, the outstanding features of the year's work are a very active and widespread discussion of current atomic theories as applied to the interpretation of chemical phenomena, some interesting and important investigations of the hydrides of boron and silicon, an extension of the work reported last year in the detailed study of germanium, and the discovery of element No. 72 with its attendant controversy as to priority in that discovery.

Valency and Atomic Theory.

The general discussion of atomic theories, comprising some two score papers or more, must be left for consideration in other Reports, but we may properly refer briefly here to those papers which are concerned primarily with "valency." The Lewis-Langmuir conception of a static atom is, for example, applied to explain the change of chemical properties by substitution,[1] the quinquevalency of boron in acidic compounds such as HBF_4 and its quadrivalency in such relatively inert substances as BF_3,NH_3 or boron nitride.[2] A series of papers has been devoted to the development of an electronic interpretation of the structure of "co-ordination" compounds in general,[3] and a further series [4] to the discussion of the polarity of double bonds, the existence, for example, in the ion $\overset{-}{F}\overset{+}{H}\overset{-}{F}$, of co-ordinated hydrogen exerting an effective (co-ordination) valency of 2, and kindred matters.

It seems possible, however, that such discussions, based as they are on a theory which is at best a half truth, are of rather limited utility. The kinetic theory of the atom, which carries general conviction of its essential truth, continues to develop [5] and now

[1] Sir J. J. Thomson, *Phil. Mag.*, 1923, [vi], **46**, 497; *A.*, ii, 682.

[2] J. Böeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 97; *A.*, ii, 406.

[3] T. M. Lowry, *Chemistry and Industry*, 1923, **42**, 224, 316, 1004, 1048; *A.*, ii, 233, 313, 750, 849; C. H. Spiers, *ibid.*, p. 534; *A.*, ii, 481.

[4] T. M. Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285; *Phil. Mag.*, 1923, [vi], **45**, 964, 1013, 1105; *A.*, ii, 480, 848; *T.*, 1923, **123**, 822, 2111.

[5] See, *e. g.*, N. Bohr and D. Coster, *Z. Physik*, 1923, **12**, 342; *A.*, ii, 110.

begins to find direct application to valency problems.[6] It seems likely to provide an explanation of the structure of molecules not inconsistent with, but a development of, that based upon the static atom models.

Special reference may be made to a paper [7] showing generally how Bohr's theory may provide a simple and adequate explanation of the existence of all co-ordinated compounds for which Werner's doctrine of sixfold symmetry is most fully established. Positive objection to the static theories has been raised [8] on the ground that they fail to explain the phenomena of stereochemistry. Although these views have been adversely criticised,[9] it seems probable that they represent the true line of advance toward a real understanding of chemical combination.

In this connexion, attention may be directed to the work of Clark and Duane,[10] who, utilising the reflection of *X*-rays characteristic of each element present in a compound, have been able to analyse separately the space distribution of each kind of atom and so determine, in a more positive manner than was hitherto possible, the real structure of solid compounds. Thus the relative positions in space of cæsium and iodine atoms in cæsium iodide and triiodide (CsI; CsI_3) have been ascertained and a step, which may prove very important, taken toward a new experimental method for the study of valency.

Atomic Weights.

Boron.—Further details have now been published of the preparation [11] and analysis [12] of the boron trichloride used for a determination of the atomic weight of boron already reported.[13]

Boron hydride, B_2H_6, prepared by heating B_4H_{10} for five hours at 95° and purified by fractional distillation at low temperatures, has been decomposed by water thus: $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$. Measurement of the volume of hydrogen produced from a known weight of the hydride gives values for the ratio $B_2H_6 : 6H_2$ corresponding to B = 10·8055 ± 0·0015.[14,15]

[6] W. Nernst, *Z. angew. Chem.*, 1923, **36**, 453; *A.*, ii, 680; N. R. Campbell, *Nature*, 1923, **111**, 569; *A.*, ii, 399.

[7] N. V. Sidgwick, *T.*, 1923, **123**, 725.

[8] S. Sugden, *T.*, 1923, **123**, 1861.

[9] T. M. Lowry, *T.*, 1923, **123**, 1866; J. D. M. Smith, *Chemistry and Industry*, 1923, **42**, 1073; *A.*, ii, 844.

[10] G. L. Clark and W. Duane, *Proc. Nat. Acad. Sci.*, 1923, **9**, 117, 126, 131; *A.*, ii, 468, 469; *Physical Rev.*, 1922, **20**, 85; *A.*, ii, 856.

[11] A. Stock and E. Kuss, *Ber.*, 1923, **56**, [*B*], 1463; *A.*, ii, 560.

[12] O. Hönigschmid and L. Birckenbach, *ibid.*, p. 1467; *A.*, ii, 559.

[13] *Ann. Reports*, 1922, **19**, 34.

[14] A. Stock and E. Kuss, *Ber.*, 1923, **56**, [*B*], 314; *A.*, ii, 157.

[15] *Idem*, *Z. anorg. Chem.*, 1923, **128**, 49; *A.*, ii, 856.

Silicon.—Preliminary results obtained by decomposition of monosilane with sodium hydroxide, Si = 28·15, 28·16, 28·14, whilst given with reserve, suggest that the current value (Si = 28·3) is too high.[14]

Analyses of silicon tetrachloride and silicon tetrabromide, purified by thorough fractional distillation under exclusion of air and at varying pressures, give as the mean of a series differing by less than 1 part in 2000 the value Si = 28·063,[16] materially lower than the accepted figure.

Titanium.—Six fractions of titanium tetrachloride, taken during the later stages of a systematic fractional distillation directed to the production of a pure specimen for precise determination of the atomic weight, were collected in bulbs, which were sealed off, weighed, and broken in dilute nitric acid. The ratio $TiCl_4 : 4Ag$ determined by nephelometric titration with weighed amounts of pure silver in the usual manner gave preliminary results ranging from 47·78 to 47·89, the rounded mean being Ti = 47·9, again appreciably lower than the accepted value (Ti = 48·1).[17]

Iron.—Using four preparations of ferric chloride, purified by sublimation in a fused silica apparatus, thirteen determinations of the ratio $FeCl_3 : 3Ag$ and twelve of the ratio $FeCl_3 : 3AgCl$ have been made. The data are concordant and give for each series the value Fe = 55·85.[18]

Nickel.—Pure nickelous chloride prepared from terrestrial nickel and from nickel extracted from the Cumpas meteorite has been used for comparative determinations of the atomic weights of terrestrial and extra-terrestrial nickel. Six and four measurements, respectively, of the ratio $NiCl_2 : 2Ag$, and two and three, respectively, of the ratio $NiCl_2 : 2AgCl$ confirmed the earlier finding that these atomic weights do not differ by an amount greater than the experimental error. The mean value now found is Ni = 58·70.[19]

Gallium.—The first precise determination of the atomic weight of gallium is now fully reported.[20] Gallium was extracted from 60 kilos. of lead residues from the distillation of zinc and, after chemical purification, the metal was deposited electrolytically, and subjected to a series of eight fractional crystallisations as metal, and the

[16] G. P. Baxter, P. F. Weatherill, and E. W. Scripture, *Proc. Amer. Acad. Arts Sci.*, 1923, **58**, 245; *A.*, ii, 412.

[17] G. P. Baxter and G. J. Fertig, *J. Amer. Chem. Soc.*, 1923, **45**, 1228; *A.*, ii, 498.

[18] O. Hönigschmid, L. Birckenbach, and R. Zeiss, *Ber.*, 1923, **56**, [*B*], 1473; *A.*, ii, 560.

[19] G. P. Baxter and F. A. Hilton, *J. Amer. Chem. Soc.*, 1923, **45**, 694; *A.* ii, 326.

[20] T. W. Richards and W. M. Craig, *ibid.*, p. 1155; *A.*, ii, 495.

purest material (m. p. 29·75°) was heated for twenty-four hours in a vacuum at 800—850° to eliminate traces of zinc, etc. Subsequently, in a sealed glass apparatus, the metal was combined with pure chlorine and the chloride was distilled in nitrogen, subjected to a series of fractional sublimations in a vacuum, and finally distilled into bulbs, which were sealed. Whilst of the usual general character, the processes adopted for the solution and analysis of the chloride, as well as the elaborate apparatus for its purification, present many interesting features described in detail in the original paper. A final series of four analyses gave values for the ratio $GaCl_3 : 3Ag$ corresponding to Ga = 69·718, 69·722, 69·707, 69·718 : *mean* 69·716, whence is deduced the rounded value Ga = 69·72 (Cl = 35·458; Ag = 107·88).

Selenium.—From determinations of the weight of a normal litre of hydrogen selenide and of the compressibility of the gas the atomic weight Se = 79·37 has been found; but this value is regarded as subject to correction when further data are obtained.[21]

Antimony.—Specimens of pure antimony were prepared from stibnites from Peru, Bolivia, Borneo, and Hungary, respectively. After fusion in hydrogen, weighed portions were dissolved in concentrated sulphuric acid, and the solution was diluted and titrated with a weighed amount of potassium bromate according to the reaction: $3SbCl_3 + KBrO_3 + 6HCl \longrightarrow 3SbCl_5 + KBr + 3H_2O$. The slight excess of antimony remaining as trichloride was estimated by titration with 0·01*N*-potassium bromate, previously standardised against the same antimony, using methyl-orange as indicator. Seven concordant determinations of the ratio $3Sb : KBrO_3$ are recorded for each sample and the atomic weights deduced are respectively Sb = 121·720, 122·374, 121·563, and 121·144. If, as is suggested, these differences are due to a variation of the isotope ratio in antimony from different localities, this may in part explain the great discordance among previous determinations of the atomic weight.[22]

Mercury.—Pure mercury was thrice distilled in a vacuum and converted into chloride or bromide, and the halides were twice sublimed and once melted in quartz vessels.

Weighed amounts of the halides were then reduced in ammoniacal solution by halogen-free hydrazine and the resulting ammonium halide was titrated nephelometrically against weighed silver in the usual manner. Both series of determinations (twelve of the ratio

[21] P. Bruylants and J. Dondeyne, *Bull. Acad. Roy. Belg.*, 1922, [v], 8, 387; *A.*, ii, 236.

[22] Sheikh D. Muzaffar, *J. Amer. Chem. Soc.*, 1923, 45, 2009; *A.*, ii, 771.

$HgCl_2$: 2Ag and eight of the ratio $HgBr_2$: 2Ag) gave the same mean result, Hg = 200·61.[23]

Similar determinations with the light and heavy fractions (d = 0·999824 and 1·000164, respectively; ordinary mercury = 1·000000) obtained by low-temperature distillation of mercury in a high vacuum gave values for the atomic weight Hg = 200·564 and 200·632, respectively.[24]

Lead.—The more volatile and less volatile end fractions of lead chloride fractionally distilled in a high vacuum by Brönstedt and von Hevesy were prepared for analysis by fusion and distillation in quartz in a current of hydrogen chloride. As a mean of ten determinations in each case of the ratio $PbCl_2$: 2Ag, they gave values for the atomic weight Pb = 207·229 ± 0·003 and Pb = 207·236 ± 0·003. The difference between these results is of the same order of magnitude as the experimental error and thus affords no evidence that any separation of the isotopes of lead has been effected.[25]

By the same methods, lead derived from Upper Katanga, Belgian Congo, gave as a mean of three determinations Pb = 206·048, whence it is concluded that the material is pure uranium lead.[26]

Richards and Putzeys have extracted lead from several minerals from the Belgian Congo, and after subjecting it to a rigorous series of recrystallisations as nitrate and chloride found, from the ratio $PbCl_2$: 2Ag determined by the methods usually employed at Harvard, Pb = 206·20.[27] They conclude that this material, which may later be available in quantity, is probably derived from a common primary deposit of uraninite and contains about 88 per cent. of uranium lead and 12 per cent. of ordinary lead.

Unclassified Phenomena.

Details have now been published of the fractionation of dry benzene reported last year, together with some new data of interest. Dried sulphur has been found to melt over a range of temperature from 116·8—118·5°. Bromine dried for ten years had m. p. — 4·5°, b. p. 118°, as compared with the values — 7·3° and 59° for bromine similarly prepared but dried only for a few days. Sulphur trioxide dried for twenty years had the m. p. 61·5° for the α-form and changed on melting to a β-form of m. p. 15·5°, the corresponding temperatures for material not specially dried being

[23] O. Hönigschmid, L. Birckenbach, and M. Steinheil, *Ber.*, 1923, **56**, [*B*], 1212; *A.*, ii, 493.

[24] *Idem, ibid.*, p. 1219; *A.*, ii, 493.

[25] O. Hönigschmid and M. Steinheil, *ibid.*, p. 1831; *A.*, ii, 764.

[26] O. Hönigschmid and L. Birckenbach, *ibid.*, p. 1837; *A.*, ii, 764.

[27] T. W. Richards and P. Putzeys, *J. Amer. Chem. Soc.*, 1923, **45**, 2954.

50° and 14·4°. The melting points of two samples of the same benzene dried for ten years and one month, respectively, were 6·0° and 5·4°. Determinations of the vapour density of ether and methyl alcohol, dried for ten years and boiling at 83° and 120°, gave the values 81·7 and 45, respectively, the normal values being 37 and 16.[28]

There has existed, apparently, some scepticism among chemists as to the reality of these phenomena and therefore it is pertinent to remark that several workers have, in the course of other investigations, confirmed the effect of intensive drying in changing the properties of liquids[29] and in inhibiting chemical reaction, for example, between hydrogen and chlorine exposed to diffused daylight, and between hydrogen and oxygen at a red heat in glass tubes.[30]

Even among chemists who accept them, these results are evidently less well known than their importance merits. A theoretical paper recently published[31] criticises adversely the view that Baker's observations are best explained by a *shift* of the inner equilibrium of liquids,[32] and propounds as new the alternative theory that drying "freezes" an existing equilibrium. As no acknowledgment is made, it would seem that the author is unaware that this theory was put forward in 1922, that the mechanism he suggests to account for a separation of the pseudo-components by distillation was fully anticipated, even before such a separation was realised,[33] and that the possible effect of conducting the drying process at various temperatures had already been foreseen.[34] It is, in fact, difficult to understand how the mere fixation of an existing equilibrium can account for the change of surface tension and for the large change of vapour pressure which have been observed.[35]

The low-temperature activation of hydrogen previously reported now found to be due to traces of oxygen, of which as little as 0·02 per cent. can cause the effects observed. It is suggested that the activity arises from traces of triatomic hydrogen formed by the combustion of the oxygen upon the surface of the platinum.[37]

[28] H. B. Baker, *T.*, 1923, **123**, 1223.

[29] H. M. Roberts and C. R. Bury, *T.*, 1923, **123**, 2037.

[30] H. Tramm, *Z. physikal. Chem.*, 1923, **105**, 356; *A.*, ii, 716; A. Coehn and H. Tramm, *Ber.*, 1923, **56**, [*B*], 455, 458, 696; *A.*, ii, 205; see also A. W. C. Menzies, *J. Amer. Chem. Soc.*, 1923, **45**, 327; *A.*, ii, 216.

[31] G. N. Lewis, *ibid.*, p. 2836.

[32] *Ann. Reports*, 1922, **19**, 36; A. Smits, *Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 266; *Rec. trav. chim.*, 1923, **42**, 826; *A.*, ii, 547, 628.

[33] A. Smits, *Z. physikal. Chem.*, 1922, **100**, 477; *A.*, 1922, ii, 358.

[34] *Idem*, "Theory of Allotropy," p. 329; *Ann. Reports*, 1922, **19**, 36.

[35] H. B. Baker, *T.*, 1922, **121**, 572; *Ann. Reports*, 1922, **19**, 36.

[37] *Ann. Reports*, 1922, **19**, 38; A. E. Mitchell and A. L. Marshall, *T.*, 1923, **123**, 2448.

After electrolysis of dilute aqueous sodium or potassium hydroxide or sulphuric acid, the cathode liquid has the property of reducing an alkaline silver solution. The reducing agent is unstable, one-half disappearing in a day, and is shown not to be ferrous hydroxide or active hydrogen.[38]

The Inert Gases.

A new method for the purification of neon, applicable to relatively large quantities, has been described, and neon so purified has been used to redetermine the critical temperature, — 228·7°, on the thermodynamic scale.[39]

By means of the mass-spectrograph, search has been made for new heavier constituents of air in the liquid oxygen residues from the evaporation of 400 tons of liquid air. The results indicate that if any gas heavier than xenon is present its amount is certainly not greater than 1 part in 10^{15} parts, and probably does not exceed 1 part in 2×10^{16} parts, of air.[40]

Group I.

Hydrogen produced by the action of hydrochloric or sulphuric acid on magnesium, or by electrolysis of aqueous sulphuric acid or potassium hydroxide using a high cathodic current density, reacts with nitrogen to form ammonia.[41] Similar active hydrogen, detected by its reaction with cold sulphur to form hydrogen sulphide, has been obtained by the burning of oxygen and hydrogen, with flame or on a platinum surface, by striking a high-tension arc between silver electrodes in hydrogen, and by the decomposition of the hydrides of sodium, potassium, and calcium.[42]

The rate of diffusion of hydrogen through nickel is an exponential function of the temperature and directly proportional to the square root of the pressure.[43] By means of a new apparatus the following values (at the temperatures stated in brackets) have been found for the specific diffusion (mg. per hour per sq. cm. for a thickness of 1 mm.) of hydrogen through a number of metals: Aluminium <0·0005 (555°); zinc 0·0012 (375°); lead 0·001 (265°); copper 0·011 (500°); 0·028 (770°); nickel 0·012 (500°); 0·100 (750°).[44]

[38] G. Tammann, *Z. anorg. Chem.*, 1923, **126**, 176; *A.*, ii, 289.
[39] C. A. Crommelin, *Rec. trav. chim.*, 1923, **42**, 814; *A.*, ii, 634.
[40] F. W. Aston, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 462; *A.*, ii, 487.
[41] A. C. Grubb, *Nature*, 1923, **111**, 600, 671; *A.*, ii, 403.
[42] Y. Venkataramaiah, *J. Amer. Chem. Soc.*, 1923, **45**, 261; *Proc. Sci. Assoc. Vizianagram*, 1922, Dec. 6; *A.*, ii, 235, 482.
[43] V. Lombard, *Compt. rend.*, 1923, **177**, 116; *A.*, ii, 570.
[44] H. G. Deming and B. C. Hendricks, *J. Amer. Chem. Soc.*, 1923, **45**, 2857.

X-Ray examination of the crystal structure of palladium shows that no abrupt change occurs on saturation with hydrogen, but that the crystal lattice expands by 2·8 per cent., in good agreement with the observed increase of 2·9 per cent. in volume. The data indicate the existence of two crystalline phases consisting of saturated and unsaturated solid solutions of hydrogen in palladium, and are inconsistent with the formation of any compound.[45]

Sodium acts on an anhydrous solution of lithium chloride in alcohol, precipitating sodium chloride and leaving in solution lithium ethoxide, which is separated by taking advantage of its diminishing solubility with rise of temperature. When treated with hydrogen sulphide, the ethoxide yields lithium hydrosulphide as a crystalline alcoholate, $2LiHS,C_2H_5{\cdot}OH$. Some evidence was obtained that the pure hydrosulphide results by the action of hydrogen sulphide upon metallic lithium suspended in ether, but the only specimen so made was accidentally subjected to the action of alcohol vapour and was thus converted into the alcoholate.[46] Metallic sodium has also been used to reduce the anhydrous chlorides of glucinum, chromium, uranium, vanadium, and zirconium in a closed steel bomb, the metals being obtained in a fairly pure state (for example, Gl 99·6 per cent., *d* 1·793, m. p. 1,370°; Cr 99·86 per cent.; *d* 6·29—6·40) and in the form of small pellets.[47]

Triammonium hydrogen sulphate, $(NH_4)_3H(SO_4)_2$, a crystalline, non-deliquescent salt, is formed by treating ammonium hydrogen sulphate with dry alcohol and washing the product with ether.[48] When mixtures of the salts are melted, sodium or ammonium hydrogen sulphate reacts with rubidium or cæsium sulphate to form the corresponding hydrogen sulphate and trisodium or triammonium hydrogen sulphate. Similarly, sodium sulphate with ammonium hydrogen sulphate or ammonium sulphate with sodium hydrogen sulphate give mixtures of the trisodium and triammonium hydrogen sulphates. These reactions were followed by determinations of the total acidity of the melts, confirmed by the results of extracting the powdered solid with dry alcohol.[49]

Ammonium hydrosulphide, obtained by interaction of ammonia and hydrogen sulphide in dry alcohol or, better, in dry ether, forms white, crystalline needles. If excess of hydrogen sulphide be used, subsequent addition of ether saturated with ammonia pre-

[45] L. W. McKeehan, *Physical Rev.*, 1923, [ii], **21**, 334; M. Yamada, *Phil. Mag.*, 1923, [vi], **45**, 241; *A.*, ii, **427**, 81.

[46] J. H. Jones and J. S. Thomas, *T.*, 1923, **123**, 3285.

[47] M. A. Hunter and A. Jones, *Amer. Electrochem. Soc.*, 1923, **44**, 35; *A.*, ii, 688.

[48] H. B. Dunnicliff, *T.*, 1923, **123**, 476. [49] *Idem*, *ibid.*, p. 731.

cipitates a white, crystalline alcoholate of ammonium sulphide, $(NH_4)_2S,C_2H_5{\cdot}OH$. If ethereal hydrogen sulphide be treated with excess of ammonia, addition of alcohol precipitates a yellow oil, $(NH_4)_2S,2NH_3$, with some transparent, apparently cubic, crystals supposed to be the normal sulphide, $(NH_4)_2S$.[50]

By the action of sulphur upon ammonium hydrosulphide in dry alcohol, orange-yellow, crystalline ammonium pentasulphide, $(NH_4)_2S_5$, is obtained. On exposure to air, this pentasulphide becomes deep red, probably through formation of the heptasulphide, $(NH_4)_2S_7$, and finally decomposes to form hydrogen sulphide, ammonia, and sulphur; when heated in a sealed tube, it yields free sulphur and ammonium disulphide, $(NH_4)_2S_2$, as a yellow oil solidifying to a yellow, crystalline mass. The enneasulphide previously described could not be obtained.[51]

Two investigations agree in finding that no definite hydrates of cupric oxide exist, dehydration taking place through a series of solid solutions,[52] but a third is held to show that, whilst this is true in the presence of water, the dry hydroxide undergoes stepwise dehydration, forming definite compounds, containing 3, 4, 6, 7, and 8 molecules of CuO for each molecule of water.[53] It should be noted, however, that the granular hydroxide, owing to its compact structure, loses water much less readily than the gelatinous hydroxides and thus tends to give misleading results.[52]

Some evidence has been obtained that the blue solutions obtained when concentrated aqueous alkali hydroxide dissolves cupric oxide or hydroxide, or is electrolysed with copper electrodes using a high current density, contain alkali salts of cupric acid of the type $M^I_2CuO_2$.[54,52]

Reaction between excess of metallic copper and stibnite begins at 500° and occurs readily at 600—700°, yielding a compound, $3Cu_2S,Sb_2S_3$. At temperatures above 700°, this compound dissociates into antimony sulphide, which sublimes, and a residue of cuprous sulphide, which may thus conveniently be prepared.[55]

Complex salts of copper and thallium are described, as follows: $Tl_2Cu(SO_4)_2,6H_2O$, blue crystals; $Tl_2Cu(SO_3)_2$, a yellow powder; $CuSO_3,3Cu_2SO_3,Tl_2SO_3$, cinnabar-red crystals soluble in aqueous ammonia to a blue solution; $Tl_4Cu(S_2O_3)_3$, a yellow, microcrystalline

[50] J. S. Thomas and R. W. Riding, *T.*, 1923, **123**, 1181.

[51] *Idem, ibid.*, p. 1726; compare Bloxam, *T.*, 1895, **67**, 777.

[52] H. B. Weiser, *J. Physical Chem.*, 1923, **27**, 501; E. Müller *et al.*, *Z. physikal. Chem.*, 1923, **105**, 73; *A.*, ii, 566, 567.

[53] L. Losana, *Gazzetta*, 1923, **53**, i, 75; *A.*, ii, 321.

[54] H. J. M. Creighton, *J. Amer. Chem. Soc.*, 1923, **45**, 1237; *A.*, ii, 492.

[55] G. Marchal, *Bull. Soc. chim.*, 1923, [iv], **33**, 597; *A.*, ii, 571.

powder.[56] Sodium thiosulphate, fused in its water of crystallisation, dissolves freshly prepared cuprous halides and cuprous thiocyanate, giving clear, colourless aqueous solutions from which are obtained crystalline complex compounds unaffected by light.[57]

Group II.

An improved method for the extraction of glucina from beryl effects decomposition of the finely ground mineral by fusion with potassium hydroxide. The powdered melt is treated with sulphuric acid and the solution is filtered from precipitated silica and adjusted to an acidity about 5*N* by addition of potassium hydroxide. On cooling, owing to the increased solubility of potassium sulphate in acid of this concentration, about 90 per cent. of the aluminium present separates as potash alum; further purification of the glucinum is effected by known methods.[58]

Interaction of anhydrous calcium chloride with sodium sulphate decahydrate for eight hours at 300° and 12·5 atms. yields a compact crystalline calcium sulphate dihydrate, $CaSO_4,2H_2O$, closely resembling natural alabaster in its texture and appearance when cut and polished.[66]

Because the variation of the cubical expansion of zinc with temperature exhibits singular points at 176° and 320°, it is inferred that this metal exists in at least three allotropic forms.[67] Details are published of a simple method for the preparation of strongly phosphorescent zinc sulphide,[68] and of the production of zinc nitride by the action of ammonia on zinc dust at 650°.[69]

Measurements of the change in specific magnetic susceptibility indicate that the dehydration of magnesium hydroxide is reversible and that of cadmium and zinc hydroxides irreversible, but that in the last case water lost is partly adsorbed by the oxide, some 2—3 per cent. being retained at 205°.[70]

A convenient apparatus for purifying mercury by air agitation, with or without the addition of the usual cleansing solutions, is described.[71]

The reduction of several metals of this group from their salts by hydrogen has been investigated. By hydrogen at 100 atms.,

[56] G. Canneri, *Gazzetta*, 1922, **52**, ii, 266; *A.*, ii, 74.
[57] G. Canneri and R. Luchini, *Gazzetta*, 1922, **52**, ii, 261; *A.*, ii, 74.
[58] H. T. S. Britton, *J. Soc. Chem. Ind.*, 1922, **41**, 349T; *A.*, ii, 28.
[66] M. Copisarow, *T.*, 1923, **123**, 796.
[67] L. Losana, *Gazzetta*, 1923, **53**, 539; *A.*, ii, 763.
[68] J. Schmidt, *Ber.*, 1922, **55**, [*B*], 3988; *A.*, ii, 73.
[69] W. J. Bently and P. L. Stern, *Science*, 1921, **53**, 143; *A.*, ii, 28.
[70] P. Pascal, *Compt. rend.*, 1923, **177**, 765; *A.*, ii, 861.
[71] A. E. Dixon and J. L. McKee, *T.*, 1923, **123**, 895.

mercurous nitrate is reduced, at 160°, to metallic mercury and a basic nitrate, possibly $2Hg_2O,N_2O_5$, and at 225°, completely to the metal; and mercuric nitrate is reduced to the mercurous salt at 170—180° and to metal at 240—250°. Cadmium nitrate yields a basic salt, $Cd(NO_3)_2,7CdO$, at 135 atms. and 220°, and crystalline metallic cadmium at 220 atms. and 275°. Zinc nitrate and sulphate were similarly reducible, but metallic magnesium could not thus be obtained.[72]

Thermal studies of the systems formed by silver nitrate with mercuric iodide and by thallous nitrate with mercuric chloride, bromide, and iodide show that no double decomposition occurs, but the following compounds are formed: $2AgNO_3,HgI_2$, yellowish-green crystals, m. p. 107°; $AgNO_3,HgI_2$, m. p. 117—118°, undergoing at 52° dimorphic change marked by change of colour from canary-yellow to orange;[73] $TlNO_3,HgCl_2$, m. p. 202·5°; $2TlNO_3,HgCl_2$, m. p. 195°; $TlNO_3,HgBr_2$, m. p. 152°.[74] A similar investigation of several binary systems of components capable of sublimation discloses the existence of two compounds of mercuric chloride with ammonium chloride: $HgCl_2,NH_4Cl$, m. p. 204°, b. p. 350°; and $HgCl_2,4NH_4Cl$, m. p. 244°, decomposing at higher temperatures.[75]

Group III.

By the use of an improved process and apparatus, whereby magnesium boride is gradually added to excess of hydrochloric acid at 40—50°, crude boron hydrides have been prepared in much greater quantity than formerly and purified by fractional condensation with liquid air. The product previously supposed to be a pure substance of the composition B_6H_{12} appears to be a mixture of B_4H_{10}, B_5H_9, and B_6H_{10} with silicon hydride. Tetraborane, B_4H_{10}, has m. p. — 120° and boils at about 18°; its density is 0·59 at — 70° and 0·56 at — 35°; even when pure, it decomposes rapidly at the ordinary temperature, giving hydrogen, diborane, and several less volatile hydrides.

Diborane has m. p. — 165·5°, b. p. about — 92°; it does not appear to dissociate below 155°; it reacts with hydrogen bromide in presence of aluminium bromide at 90°, forming the very unstable monobromodiborane.

The hydride, B_5H_9, best obtained by fractionation of the pro-

[72] W. Ipatiev and A. Starynkevitsch, *Ber.*, 1923, **56**, [*B*], 1663; *A.*, ii, 639.

[73] A. G. Bergmann, *J. Russ. Phys. Chem. Soc.*, 1921, **53**, 181; *A.*, ii, 636.

[74] A. G. Bergmann, T. A. Henke, and F. M. Isaïkin, *ibid.*, 1922, **54**, 466; see also *ibid.*, 1922, **54**, 200; *A.*, ii, 568, 764.

[75] E. Jänecke, *Rec. trav. chim.*, 1923, **42**, 740; *A.*, ii, 640.

ducts of decomposition of tetraborane at 100°, is a colourless, mobile liquid, m. p. — 46·9°; it has an extremely unpleasant odour and is the noxious constituent of crude boron hydrides. It is fairly stable, but is slowly hydrolysed by water at 90°, forming hydrogen and boric acid.

The hydride B_6H_{10} is a colourless, refractive liquid, m. p. — 65·1°, hydrolysable, as is B_5H_9; when kept at the ordinary temperature in daylight, it decomposes, yielding mainly a yellow, crystalline, solid hydride.

Analysis of these compounds is effected by thermal decomposition into boron and hydrogen at a fairly high temperature; at and below 300° they exhibit differences in stability and in the nature of the products of decomposition, for details of which the original paper should be consulted.[76]

Almost quantitative yields of boron trichloride are obtained by the action of chlorine upon ferro-boron at 500°.[77]

By maintaining a temperature gradient in systems of borax and boric oxide during cooling it is possible to ensure that at some point in the mass conditions are such as to permit crystallisation. Thus the fusion diagram of this system has been constructed and found to indicate the existence of two new compounds : $Na_2O,3B_2O_3$, m. p. 694°, and $Na_2O,4B_2O_3$, m. p. 783°, forming solid solutions with each other and with boric oxide.[78]

Evidence from the cooling curves and micro-structure of aluminium–copper alloys containing 14—21 per cent. of aluminium shows that the compound $AlCu_2$, melting with decomposition at 1,016°, probably undergoes change to another crystalline form, without decomposition, on cooling to about 700°.[79] A similar study of the system aluminium–iron indicates the existence of an endothermic compound, Al_3Fe, and, with lower proportions of iron, a stable phase markedly different in properties from the adjoining alloys but variable in composition.[80] Aluminium–titanium alloys with up to 30 per cent. of the latter metal contain hard crystals of the compound Al_4Ti, m. p. 1,325°, and immiscible with aluminium.[81]

Aqueous solutions of aluminium chloride and sodium silicate react to form a precipitate of the composition $2Al_2O_3,3SiO_2$ which

[76] A. Stock and E. Kuss, *Ber.*, 1923, **56**, [*B*], 789; *A.*, ii, 408.

[77] C. Mazzetti and F. De Carli, *Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 119; *A.*, ii, 67.

[78] I. F. Ponomarev, *J. Russ. Phys. Chem. Soc.*, 1917, **49**, 229; *A.*, ii, 415.

[79] D. Stockdale, *Trans. Faraday Soc.*, 1923, **19**, 135; *A.*, ii, 766.

[80] N. Kurnakov, G. Urasov, and A. Grigoriev, *Z. anorg. Chem.*, 1922, **125**, 207; *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 270; *A.*, ii, 75.

[81] E. van Erckelens, *Metall und Erz*, 1923, **20**, 206; *A.*, ii, 569.

adsorbs silica and in presence of sufficient silicic acid is converted into the compound $Al_2O_3,2SiO_2$, analogous to kaolin, $Al_2O_3,2SiO_2,2H_2O$. Investigations of the *X*-ray spectra of these products and of the course of their dehydration indicate that the first is amorphous and that, under the conditions of experiment one compound only, $Al_2O_3,2SiO_2,xH_2O$, is formed.[82]

Metallic lanthanum was prepared by electrolysing fused anhydrous lanthanum chloride containing small proportions of sodium chloride and potassium fluoride, in a graphite cell which served as cathode, using currents of 40—50 amps. at 7—8 volts. After being washed with water, to remove adhering salt and to decompose carbide with which it was contaminated, the product was remelted under calcium chloride in a graphite crucible and used for determination of the following properties: m. p. 826°; d^{15} 6·16; Brinnell hardness (500 kg.) 37; heat of combustion 1645 cal./gm.; kindling temperature 445°. The metal is not ductile, is easily oxidised even by dry air, but is not pyrophoric in the pure state or when alloyed with iron.[83]

The action of water upon the product of fusion of lanthanum oxide with sodium carbonate gives only the double carbonate, $La_2(CO_3)_3,Na_2CO_3,12H_2O$; hence it appears that the various lanthanates of sodium, potassium, and barium formerly described [84] do not exist.[85]

Similar crystalline double salts are formed by sodium carbonate with the carbonates of cerium, praseodymium, neodymium, and samarium.[86] A series of triple nitrites of cobalt, nickel, or copper with an alkali metal and a metal of the cerium or yttrium group has been described.[87]

Investigation of the emission spectra of rare-earth fractions containing terbium, dysprosium, and gadolinium is reported to indicate the presence of a new element, giving a well-defined and characteristic line spectrum, for which the name *welsium* is proposed.[88]

Group IV.

Vitreous carbon, giving an *X*-ray spectrum containing the lines of both diamond and graphite, is obtained by exposing a heated,

[82] R. Schwarz and A. Brenner, *Ber.*, 1923, **56**, [*B*], 1433; *A.*, ii, 569.

[83] H. C. Kremers and R. G. Stevens, *J. Amer. Chem. Soc.*, 1923, **45**, 614; *A.*, ii, 322.

[84] C. Baskerville and G. F. Catlett, *A.*, 1904, ii, 260.

[85] F. Zambonini and G. Carobbi, *Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 53; *A.*, ii, 765.

[86] *Idem*, *ibid.*, p. 125; *A.*, ii, 863.

[87] V. Cuttica and F. Gallo, *Gazzetta*, 1923, **53**, i, 374; *A.*, ii, 689.

[88] J. M. Eder, *Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Klass.* 1922, [iia], **131**, 199; *A.*, ii, 47.

chemically inert surface to the luminous flames of certain aliphatic hydrocarbons. It is very pure (C = 99·06 per cent.), has d_4° 2·07 and a low electrical conductivity, and that prepared at 1,300° is harder than carborundum.[89] Pure graphite has been obtained by carbonising filaments of artificial silk, first in coal gas at 500°, then in hydrogen at 2,200—2,500°, and maintaining them at 1,500—2,000° in the vapour of hexachlorobenzene, carbon tetrachloride, or light petroleum, etc., at low pressures, or in the last two cases in the liquid state, until the cross section of the filament had very greatly increased. After heating at 3,500° in carbon monoxide, such filaments have all the properties of pure graphite and can be bent like lead.[90] Carbon produced by heating graphitic acid has d_4° 2·215 and therefore is probably pure graphite.[91]

By heating purified water-gas to 200—300° at atmospheric pressure in contact with nickel, the reaction $2CO + 2H_2 \rightleftarrows CO_2 + CH_4$ occurs to a considerable extent, and it is suggested that the process may find technical application in the manufacture of methane or in the partial substitution of methane for carbon monoxide in towns gas.[92]

Some interesting work upon the hydrides of silicon is reported. From the study of reactions in which alcohol is in part substituted for water, it is inferred that when magnesium silicide is decomposed by hydrochloric acid about 10 per cent. reacts as follows :

$$Mg{:}Si{:}Mg + 2H{\cdot}OH \longrightarrow H_2Si(Mg{\cdot}OH)_2,$$

and the remainder yields silica and hydrogen, probably by the reaction

$$Mg_2Si + 4HCl + 2H_2O \longrightarrow 2MgCl_2 + SiO_2 + 4H_2.$$

Production of silanes probably occurs by further hydrolysis of the first product, for example, thus : $SiH_2(Mg{\cdot}OH)_2 + 2H{\cdot}OH \longrightarrow 2Mg(OH)_2 + SiH_4$, and $SiH_2(Mg{\cdot}OH)_2 + 4HCl \longrightarrow 2MgCl_2 + H_2O + SiH_2O + 2H_2$.[93] Failure attended attempts to effect regulated oxidation of silane by admixture with oxygen, air, or air diluted with nitrogen under greatly reduced pressure and at — 70° to — 140°.[94]

Disiloxan, $(SiH_3)_2O$, is but slightly decomposed by heating at

[89] K. A. Hofmann and C. Röchling, *Ber.*, 1923, **56**, [*B*], 2071; *A.*, ii, 757.
[90] M. Pirani and W. Fehse, *Z. Elektrochem.*, 1923, **29**, 168; *A.*, ii, 317.
[91] R. M. Burns and G. A. Hulett, *J. Amer. Chem. Soc.*, 1923, **45**, 572; *A.*, ii, 317.
[92] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 25; *A.*, ii, 307.
[93] R. Schwarz and E. Konrad, *Ber.*, 1922, **55**, [*B*], 3242; A., 1922, ii, 846.
[94] A. Stock and C. Somieski, *ibid.*, p. 3961; *A.*, ii, 67.

400°, but phosphoric oxide decomposes it at the ordinary temperature, forming chiefly monosilane, hydrogen, and polymeric prosiloxan, probably by hydrolysis of the type: $(SiH_3)_2O + H_2O \longrightarrow 2SiH_2O + 2H_2$.[95]

Disilane at 500° suffers decomposition, analogous to the cracking of hydrocarbons, producing silicon, hydrogen, and monosilane. Monochlorosilane and hydrogen sulphide at 150° in presence of aluminium chloride yield hydrogen, dichloromonosilane, and a volatile compound containing sulphur, possibly $SiH_2 \cdot HS$ or $(SiH_3)_2S$. Dichloromonosilane reacts with sodium amalgam to give monosilane and the unsaturated, yellow polymerised hydride $(SiH)_x$.[96]

Trichloromonosilane, prepared from copper silicide and hydrogen chloride at 300°, and purified by fractional distillation in a vacuum, has m. p. — 126·5°, b. p. 31·8°, d^0 1·35. It is remarkably stable to heat and unaffected by aluminium chloride at 175°; at 900°, it decomposes almost quantitatively into silicon, hydrogen, hydrogen chloride, and silicon tetrachloride. It is immediately decomposed by water, yielding solid non-volatile silicoformic anhydride, $[HSiO]_2O$; it reacts with sodium amalgam readily, probably according to the scheme $xSiHCl_3 + 3xNa \longrightarrow 3xNaCl + (SiH)_x$; and with ammonia, in the gaseous phase at low pressures or in the liquid state at low temperatures, it forms an imide, $2SiHCl_3 + 9NH_3 \longrightarrow [SiH(NH)]_2NH + 6NH_4Cl$, which decomposes on heating to yield mainly ammonia and SiHN.[97]

Trisilane reacts with chloroform (4·3 mols.) at 50° to form mixtures of isomeric chlorotrisilanes according to the schemes $Si_3H_8 + 4CHCl_3 \longrightarrow Si_3H_4Cl_4 + 4CH_2Cl_2$; and $Si_3H_8 + 5CHCl_3 \longrightarrow Si_3H_3Cl_5 + 5CH_2Cl_2$.[98] Trisilane (silicopropane) has d_4^0 0·743, m. p. — 117·4°, b. p. 53°; tetrasilane (silicobutane) has d_4^0 0·825, m. p. *circa* — 90°, b. p. 109°.[99]

Reference may here be made to Sosman's theory [1] that all the forms of silica contain the same atom triplet, $>Si<^{O}_{O}$, aggregated into chains by linking of the silicon atoms. Liquid and vitreous silica are characterised by mere assembly of such chains in juxtaposition; the crystalline forms of silica (cristobalite, tridymite, and quartz) by their systematic linking *via* the oxygen atoms.

Investigation of the reduction of the tetrachlorides of titanium and zirconium by sodium amalgam, magnesium, zinc, aluminium,

[95] A. Stock and C. Somieski, *Ber.*, 1923, **56**, [*B*], 132; *A.*, ii, 160.
[96] *Idem*, *ibid.*, p. 247; *A.*, ii, 160.
[97] A. Stock and F. Zeidler, *ibid.*, p. 986; *A.*, ii, 412.
[98] A. Stock and P. Stiebeler, *ibid.*, p. 1087; *A.*, ii, 486.
[99] A. Stock, P. Stiebeler, and F. Zeidler, *ibid.*, p. 1695; *A.*, ii, 633.
[1] R. B. Sosman, *J. Franklin Inst.*, 1922, **194**, 741; *A.*, ii, 69.

tin, arsenic, phosphorus, etc., has shown that reduction by aluminium at about 250° affords a convenient means for the preparation of the trichlorides, from which excess of tetrachloride and aluminium chloride can be removed by distillation. Titanium trichloride thus prepared is a bright violet, non-crystalline powder subliming at 425°/<1 mm. to form dark violet, prismatic crystals; it is very sensitive to oxygen and moisture, and dissociates at 450° to form the volatile tetrachloride and a black residue of the dichloride, which is very reactive, takes fire in moist air, and decomposes water with evolution of hydrogen.[2] Zirconium trichloride, obtained as a brown, microcrystalline solid, d^{18} 3·0, and the black dichloride formed by its dissociation at 330° generally resemble the titanium compounds.[3]

The greater part (90—95 per cent.) of the silica present in zirkite may be eliminated by heating at 2,200° with carbon in the electric furnace, and a crude zirconia may thus be obtained which is a valuable refractory material. Zirconium carbide is infusible in a 40—50 kw. arc, but must be protected against oxidation.[4]

Investigation of the system thorium oxide–chromic anhydride–water at 25° discloses the existence of two solid phases, the normal chromate, $Th(CrO_4)_2,3H_2O$, and a microcrystalline acid chromate, $Th(CrO_4)_2,CrO_3,3H_2O$, stable in presence of dichromate or chromic acid, but decomposed by water. The normal salt is conveniently prepared by precipitating a boiling acid solution of thorium nitrate with potassium chromate.[5]

Germanium hydride, prepared by the action of hydrochloric acid upon an alloy of germanium and magnesium, was condensed at −185° and purified by sublimation; it had m. p. −165°; b. p. −126°/757 mm. When decomposed by heat, it gave 2·05 times its volume of hydrogen; it contained 94·70 per cent. Ge and 5·29 per cent. H (calc., Ge = 94·73 and H = 5·27 per cent.); determinations of its vapour density gave the molecular weight 76·93; therefore the hydride is proved to be GeH_4.[6]

An improved method is described for the extraction of germanium.[7] Metallic germanium is best prepared by reducing small quantities of the dioxide (2 grams) in hydrogen at 540° and fusing the powder under sodium chloride at 980—1,000°; with larger

[2] O. Ruff and F. Neumann, *Z. anorg. Chem.*, 1923, **128**, 81; *A.*, ii, 868.

[3] O. Ruff and R. Wallstein, *ibid.*, p. 96; *A.*, ii, 868.

[4] J. G. Thompson, *J. Physical Chem.*, 1922, **26**, 812; *A.*, ii, 79.

[5] H. T. S. Britton, *T.*, 1923, **123**, 1429.

[6] R. Schenck [with A. Imker], *Rec. trav. chim.*, 1922, **41**, 569; *A.*, 1922, ii, 855.

[7] L. M. Dennis and E. B. Johnson, *J. Amer. Chem. Soc.*, 1923, **45**, 1380; *A.*, ii, 570.

amounts of oxide, reduction is incomplete and some germanium volatilises. When free from oxide, the metal does not lose weight in an atmosphere of hydrogen at 800°, but it volatilises in a current of the gas. Germanium melts at 958·5°, expands on solidification, and has $d^{20°}_{20°}$ 5·35; it is very brittle and has a hardness of 6·25 on Moh's scale. A fused button exhibits a superficial resemblance to antimony, containing elongated crystals about 3 cm. long, some bounded by octahedral faces and often covered with dendritic branches. In thermoelectric power and electrical resistance germanium conforms to its position in the Periodic System.[8] Evidence was obtained that germanium when heated undergoes a gradual molecular inversion through two or more modifications between 117° and 560°.

At 730° in oxygen, germanium is partly oxidised to a mixture of the dioxide and germanous oxide; at higher temperatures, the latter volatilises, thus preventing complete oxidation. Hydrogen sulphide has no action on germanium below 200° and but slight action until dissociation sets in, when the reaction between free sulphur and germanium produces germanous sulphide. Sulphur dioxide at 510—530° similarly yields germanium dioxide and disulphide.

At temperatures up to 90°, germanium is not attacked by water, 50 per cent. aqueous sodium hydroxide, 1 : 1-hydrochloric acid, concentrated hydrochloric acid or nitric acid, or 1 : 1-sulphuric acid, and but little by concentrated sulphuric acid or 19*N*-hydrofluoric acid. Dilute nitric acid oxidises the metal superficially to the dioxide, and 3 per cent. hydrogen peroxide slowly converts the metal into dioxide and dissolves it. A number of other reactions are described in the original communication.[9]

Germanium reacts with iodine vapour at 250—360°, yielding the tetraiodide, GeI_4, and a little germanous iodide, GeI_2, which forms yellow, hexagonal crystals. Germanium tetraiodide crystallises in regular octahedra, $d^{26°}_{26°}$ 4·3215, melting sharply at 144° to a ruby-red liquid; the colour of the solid varies with temperature from canary-yellow at — 185° to ruby-red at the melting point. It sublimes unchanged just above the melting point, but at 440° dissociates reversibly into germanous iodide and iodine. It is unchanged by several months' exposure to air or by immersion in cold, concentrated sulphuric acid, but dissolves slowly in 25 per cent. aqueous potassium hydroxide and in concentrated hydrochloric acid, and is decomposed by a small quantity of water.

[8] C. C. Bidwell, *Physical Rev.*, 1922, **19**, 447.

[9] L. M. Dennis, K. M. Tressler, and F. E. Hance, *J. Amer. Chem. Soc.*, 1923, **45**, 2033; *A.*, ii, 769.

It is soluble in carbon tetrachloride, carbon disulphide, and many organic solvents.[10]

A complete thermal and micrographic study of the system tin–arsenic shows that these metals alloy in all proportions and form two compounds, SnAs and Sn_3As_2.[11] The form of the melting-point curve for mixtures of stannic bromide and iodide and analyses of the solid phases separating from these mixtures show that the mixed halides often described in the literature do not, in fact, exist.[12]

Magnetic analysis of the stannic acids confirms the view that they are not definite compounds.[13]

Element No. 72.

In January, Coster and Hevesy announced [14] that, in examining the *X*-ray spectra of a number of minerals, they had detected six lines clearly attributable to the element of atomic number 72. They further argued that the lines observed by Dauvillier [15] in a rare-earth preparation were very faint, were only two in number, differed by about 4X.u(1X.u = 10^{-11} cm.) in wave-length from the corresponding lines (Lα and Lβ) now observed, and could not certainly be identified with the new element Urbain claimed [16] to have detected in the same material by optical and magnetic examination and named *celtium*. Coster and Hevesy therefore exercised the prerogative of discoverers and proposed the name *hafnium* for element No. 72. Urbain and Dauvillier replied [17] asserting that the lines observed by them were identical with those observed by Coster and Hevesy, quoting cases in support of their contention that it is possible for a quadrivalent element to be present in the mother-liquors of rare-earth fractionation (a contention supported by the observation that thorium molybdate, $Th(MoO_4)_2$, is isomorphous and miscible with cerous molybdate [18]), and claiming priority for the name celtium. Coster and Hevesy in answer pointed out [19] that there is no difficulty in effecting chemical separation of hafnium from accompanying rare earths and that it does not appear to yield

[10] L. M. Dennis and F. E. Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 2854; *A.*, ii, 172.

[11] Qasim Ali Mansuri, *T.*, 1923, **123**, 214.

[12] M. G. Räder, *Z. anorg. Chem.*, 1923, **130**, 325; *A.*, ii, 867.

[13] P. Pascal, *Compt. rend.*, 1922, **175**, 1063; *A.*, ii, 79.

[14] D. Coster and G. Hevesy, *Nature*, 1923, **111**, 79; *A.*, ii, 80.

[15] *Ann. Reports*, 1922, **19**, 52.

[16] G. Urbain, *A.*, 1911, ii, 115.

[17] *Idem*, *Compt. rend.*, 1923, **176**, 469; G. Urbain and A. Dauvillier, *Nature*, 1923, **111**, 218; *A.*, ii, 171.

[18] F. Zambonini, *Atti R. Accad. Lincei*, 1923, [v], **32**, i, 518; *A.*, ii, 691.

[19] D. Coster and G. Hevesy, *Nature*, 1923, **111**, 252; *A.*, ii, 171.

the optical spectrum assigned by Urbain to celtium.[20] Further controversy on this matter has continued throughout the year,[21] and the question cannot yet be regarded as settled. One hopes that some means may be found to avoid in this case such confusion as still persists in the cases of glucinum and columbium.

It is clear that our knowledge of the properties of this element is almost wholly due to the work of Coster and Hevesy whose name, hafnium, will therefore be adopted here.

Both the *X*-ray [22] and optical spectra [23] of hafnium have been fully investigated, and the proportion of this element in any mixture may be estimated by measuring the intensity of its lines in the *X*-ray spectrum as compared with that of lines due to known amounts of tantalum (atomic number 71) added to the specimen.[24] Thus it has been found that all zirconium minerals contain hafnium, although in very varying amounts: the oxides generally contain 1—2 per cent., the silicates, for example, zircon, 2—6 per cent., whilst alvite from Kragerö, Norway, contains 34 per cent. of zirconia and 16 per cent. of hafnia.[25] Hafnium does not occur in typical thorium minerals free from zirconium, such as Ceylonese thorianite or Norwegian orangite and thorite, or in titanium minerals such as rutile and ilmenite; but zirconia extracted on the large scale from fergusonite and euxenite contains 5—6 per cent. of hafnium.

Chemically, hafnium exhibits a close general similarity to zirconium, with which it is readily separated from the rare earths and thorium by the usual methods. Separation of hafnium and zirconium from each other is best effected by fractional crystallisation of aqueous solutions of the double fluorides with potassium formed by fusing the material with potassium hydrogen fluoride. Hafnium is more basic than zirconium, and its phosphate is appreci-

[20] H. M. Hansen and S. Werner, *Nature*, 1923, **111**, 322; *A.*, ii, 200.

[21] *For Celtium:* A. Dauvillier, *Compt. rend.*, 1923, **176**, 676; *A.*, ii, 200; M. de Broglie and J. Cabrera, *ibid.*, p. 433; *A.*, ii, 200; G. Urbain, *Chemistry and Industry*, 1923, **42**, 764; *A.*, ii, 645; Anon., *ibid.*, p. 784; *A.*, ii, 692; B. Brauner, *ibid.*, p. 884; *A.*, ii, 692. *For Hafnium:* H. M. Hansen and S. Werner, *Nature*, 1923, **111**, 461; *A.*, ii, 426; D. Coster and G. Hevesy, *ibid.*, p. 462; *A.*, ii, 426; H. S. King, *ibid.*, 1923, **112**, 9; *A.*, ii, 645.

[22] D. Coster, *Phil. Mag.*, 1923, [vi], **46**, 956; *A.*, ii, 807; A. Žáček, *Z. Physik*, 1923, **15**, 31; *A.*, ii, 449.

[23] J. Bardet, *Compt. rend.*, 1923, **176**, 1711; *A.*, ii, 449; H. M. Hansen and S. Werner, *Nature*, 1923, **112**, 618; *A.*, ii, 807.

[24] D. Coster, *Chem. News*, 1923, **127**, 65; D. Coster and G. Hevesy, *Nature*, 1923, **111**, 182; *A.*, ii, 171.

[25] G. Hevesy and V. T. Jantzen, *T.*, 1923, **123**, 3218; see also V. M. Goldschmidt and L. Thomassen, *Norsk Geologisk Tidsskrift*, 1923, **7**, 61; *A.*, ii, 174.

ably less soluble in concentrated acids than is zirconium phosphate, but these differences do not afford a convenient means of separation. From preparations rich in hafnium, zirconium may be separated by dissolving the oxychlorides in alcohol and adding ether, when the less soluble basic salt, $Zr_2O_3Cl_2,5H_2O$, is precipitated.

A preliminary determination, using hafnium containing 5—6 per cent. of zirconium, indicates an atomic weight between 178·4 and 180·2.[26]

Group V.

Details have been given of a more convenient process for the preparation of potassium hydroxylamine*iso*disulphonate,[27] and of a technique for the preparation of hydrazine by Raschig's method.[28]

Nitric oxide and hydrogen chloride at — 180° yield a solid having an intense purple colour and melting at about — 150° to a purple liquid with an electrical conductivity about that of 0·01*N*-potassium chloride solution. The vapour pressure of the substance is not appreciably less than that of pure nitric oxide at the same temperature, whence it is inferred that the complex is exceptionally unstable and probably (in view of its colour) of the type $[NOH]^+Cl^-$.[29]

A study of the absorption spectra of nitrosylsulphuric acid and of the complex compounds of copper sulphate and ferrous sulphate with nitric oxide shows that appreciable quantities of this acid remain undecomposed on dilution with water to 50 per cent.; thus one of the fundamental assumptions of Raschig's theory of the chamber process is invalidated.[30]

Certain properties of ammonia have been redetermined, using fifteen carefully purified samples containing less than 0·0001 per cent. of non-condensible gases and less than 0·003 per cent. of water, as follows: freezing point, — 77·7°; vapour pressure at the freezing point, 45·2 mm.; density of the solid at — 79°, 0·817 gm./c.c.; at — 185°, 0·836 gm./c.c.[31] The boiling point is — 33·41° $\pm$ 0·1°.[32]

When cooled, normal solutions of potassium hypochlorite and ammonia are mixed and distilled under reduced pressure at 30—40°,

[26] G. Hevesy, *Chem. News*, 1923, **127**, 33; *A.*, ii, 570; *Chemistry and Industry*, 1923, **42**, 929; *A.*, ii, 769; *Ber.*, 1923, **56**, [*B*], 1503; *A.*, ii, 645.

[27] F. Raschig, *Ber.*, 1923, **56**, [*B*], 206; *A.*, ii, 161; see also W. L. Semon, *J. Amer. Chem. Soc.*, 1923, **45**, 188; *A.*, ii, 155.

[28] R. A. Joyner, *T.*, 1923, **123**, 1114.

[29] W. H. Rodebush and T. O. Yntema, *J. Amer. Chem. Soc.*, 1923, **45**, 332; *A.*, ii, 237.

[30] H. I. Schlesinger and A. Salathe, *ibid.*, p. 1863; *A.*, ii, 673.

[31] E. C. McKelvy and C. S. Taylor, *U.S. Bur. Standards, Sci. Paper* 465, 1923, 655; *A.*, ii, 557.

[32] F. W. Bergstrom, *J. Physical Chem.*, 1922, **26**, 876; *A.*, ii, 56.

the distillate contains 10—12 per cent. of monochloroamine, NH_2Cl. This substance readily decomposes, even at 0°, but it is greatly stabilised in solution by the presence of very small amounts of ammonia; and by desiccating the vapours of such a solution over anhydrous potassium carbonate and condensing the residue at — 180°, pure chloroamine is obtained as a colourless, crystalline substance, m. p. — 66°; it decomposes suddenly at about — 50°, forming nitrogen, chlorine, and ammonium chloride, and its liability to explode violently under these conditions rendered further investigation impracticable.[33]

Ammonia reacts with sulphur monochloride in cold chloroform solution, yielding mainly nitrogen sulphide, N_4S_4, which may be precipitated by adding alcohol; but the mother-liquors on concentration yield nitrogen pentasulphide, N_2S_5, and hexasulphamide, S_6NH_2, crystallising in colourless, square plates, m. p. 105°.[34]

Sodamide in liquid ammonia solution, when treated with amalgamated aluminium, forms a definite, crystalline compound which, since it loses one molecule of ammonia above 90° in a vacuum, may be formulated $Al(NH_2)_2NHNa,NH_3$.[35]

Further work is recorded upon the additive compounds formed by ammonia with the halides of the alkali metals, calcium, strontium, barium, bivalent tin, and lead.[36]

Thenard's " black phosphorus " has been shown to be a colloidal suspension of mercury in phosphorus and distinct from the true black phosphorus prepared by Bridgman.[37]

Several phosphides have been prepared by the action of hydrogen phosphide upon solutions of metallic salts: mercurous sulphate in dilute sulphuric acid yields black, amorphous mercurous phosphide, PHg_3; mercuric chloride in ether gives pure mercuric phosphide, P_2Hg_3, as a dark brown solid attacked by warm water, alkalis, and dilute acids with liberation of phosphine; alcoholic lead acetate and ammoniacal cadmium sulphate give black, flocculent precipitates of the phosphides, P_2Pb_3 and P_2Cd_3, which are even less stable.[38]

Phosphorus trichloride is obtained in almost quantitative yield by heating calcium phosphates at 1,000° with sulphur chloride

[33] W. Marckwald and M. Wille, *Ber.*, 1923, **56**, [*B*], 1319; *A.*, ii, 558.

[34] A. K. Macbeth and H. Graham, *Proc. Roy. Irish Acad.*, 1923, **36**, 31; *A.*, ii, 855.

[35] F. W. Bergstrom, *J. Amer. Chem. Soc.*, 1923, **45**, 2788.

[36] G. F. Hüttig, *Z. anorg. Chem.*, 1922, **123**, 31; **124**, 322; **125**, 269; *A.*, 1922, ii, 849; 1923, ii, 28, 72; W. Biltz *et al.*, *ibid.*, 1922, **124**, 230; 1923, **127**, 1; **129**, 1; *A.*, 1922, ii, 851; 1923, ii, 760, 867.

[37] C. H. Hall, *J. Amer. Chem. Soc.*, 1923, **45**, 67; *A.*, ii, 156.

[38] A. Brukl, *Z. anorg. Chem.*, 1922, **125**, 256; *A.*, ii, 75.

and a catalyst such as silica;[39] and its oxidation to the oxychloride may conveniently be effected by passing a current of chlorine through the liquid and dropping in an equivalent quantity of water.[40]

The mode of reduction of silver nitrate by hypophosphorous acid affords further evidence in support of the hypothesis that an active tervalent form of the acid exists,[41] and a detailed study of the reaction between phosphorous acid and iodine, which proves to be much more complex than previous workers had supposed, provides data which can best be explained on the assumption that phosphorous acid too can exist in an active and an inactive form, the complete change being represented :[42]

$$H_3PO_4 + 2HI \xleftarrow{I_2+H_2O} \underset{\text{(normal)}}{H_3PO_3} \rightleftharpoons \underset{\text{(active)}}{H_3PO_3} \xrightarrow{I_2+H_2O} H_3PO_4 + 2H^+ + 3I^-.$$

Crystalline tetraphosphoric acid, $H_6P_4O_{13}$, m. p. 34°, $d^{15°}$ 1·8886, hitherto known only in the form of its salts, is obtained from phosphoric acid by adding phosphoric oxide sufficient to make the total P_2O_5 520 per cent. of the water present and allowing the syrupy liquid to stand some days.[43] Diphosphatoferric acid,

$$[Fe(PO_4)_2]H_3,2\tfrac{1}{2}H_2O,$$

has been obtained by the action of excess of phosphoric acid on aqueous ferric chloride.[44]

Pure tantalic acid has been shown to be non-volatile when heated in oxygen or on evaporation of its solution in hydrogen fluoride, and new double fluorides of tantalum with hydrogen, ammonium, and barium are described.[45]

Arsenic trichloride, tribromide, and tri-iodide may conveniently be prepared by treating a heated mixture of arsenious oxide and powdered sulphur with the appropriate halogen.[46]

Examination of the alleged antimonious hydroxides prepared from barium antimonyl tartrate and sulphuric acid, from tartar emetic and hydrochloric acid, and by the action of alkali carbonates or hydroxides on antimony trichloride,[47] and of specimens of hydrated antimony pentoxide prepared in various ways,[48] shows that no stable hydroxide exists in either case.

[39] P. P. Budnikov and E. A. Shilov, *J. Soc. Chem. Ind.*, 1923, **42**, 378T; *A.*, ii, 763.

[40] A. A. Vanscheidt and V. Michailovitsch, *J. Russ. Phys. Chem. Soc.*, 1920, **52**, 270; *A.*, ii, 559.

[41] A. D. Mitchell, *T.*, 1923, **123**, 629; compare *Ann. Reports*, 1922, **19**, 53.

[42] *Idem*, *T.*, 1923, **123**, 2241.

[43] M. A. Rakusin and A. A. Arsenéev, *Chem. Ztg.*, 1923, **47**, 195; *A.*, ii, 237.

[44] L. Dede, *Z. anorg. Chem.*, 1922, **125**, 28; *A.*, ii, 31.

[45] O. Hahn and K. F. Puetter, *ibid.*, 1923, **127**, 153; *A.*, ii, 773.

[46] G. Oddo and U. Giachery, *Gazzetta*, 1923, **53**, i, 56; *A.*, ii, 316.

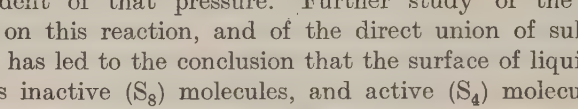
[47] C. Lea and J. K. Wood, *T.*, 1923, **123**, 259.

[48] G. Jander and A. Simon, *Z. anorg. Chem.*, 1923, **127**, 68; *A.*, ii, 772.

Dissolution of bismuth in 70 per cent. perchloric acid is found to be attended by serious danger of explosion, but it may safely be dissolved in 40 per cent. acid. This solution, on evaporation in a vacuum, deposits small, hexagonal tablets of the salt $Bi(ClO_4)_3,5H_2O$, readily hydrolysable to the bismuthyl perchlorate, $(BiO)ClO_4,3H_2O$, which changes to a monohydrate, $(BiO)ClO_4,H_2O$, forming hygroscopic, rhombohedral crystals. By solution of antimony oxide in hot 70 per cent. perchloric acid, small needles of antimonyl perchlorate, $(SbO)ClO_4,2H_2O$, are obtained.[49]

Group VI.

Direct union of sulphur and hydrogen at temperatures below 400° occurs by way of two reactions: (*a*) a gaseous reaction proportional in velocity to the pressure of hydrogen, and (*b*) a surface reaction independent of that pressure. Further study of the effect of oxygen on this reaction, and of the direct union of sulphur and oxygen, has led to the conclusion that the surface of liquid sulphur contains inactive (S_8) molecules, and active (S_4) molecules which adsorb oxygen and then split off sulphur dioxide according to the following scheme :[50]



Both hydrogen disulphide and hydrogen trisulphide dissolve large quantities of sulphur, and the variation of solubility with temperature shows a well-defined break at — 1·45° when the composition of the liquid phase approximates very closely to that of hydrogen hexasulphide, H_2S_6.[51]

Measurements of the viscosity of gaseous sulphur dioxide indicate molecular dimensions which accord with the value calculated for a molecule $S<^{O}_{O}$, but not with that deduced for Langmuir's model, O:S·O.[52]

Further studies have been made of the oxidising action of sulphur dioxide. The observed velocities of reaction between ferrous phosphate and sulphur dioxide in phosphoric acid solution according to the scheme

$$4Fe(H_2PO_4)_2 + 4H_3PO_4 + SO_2 \rightleftharpoons 4Fe(H_2PO_4)_3 + 2H_2O + S$$

[49] F. Fichter and E. Jenny, *Helv. Chim. Acta*, 1923, **6**, 225; *A.*, ii, 245.

[50] R. G. W. Norrish and E. K. Rideal, *T.*, 1923, **123**, 696, 1689, 3202.

[51] J. H. Walton and E. L. Whitford, *J. Amer. Chem. Soc.*, 1923, **45**, 601; *A.*, ii, 315.

[52] A. O. Rankine and C. J. Smith, *Proc. Physical Soc.*, 1922, **35**, 33; *A.*, ii, 66.

are explained [53] on the assumption that the primary change produces an active reducing compound, possibly a polythionic acid,[54] which later decomposes irreversibly, depositing sulphur. The oxidising and reducing actions of sulphur dioxide on the sulphates of molybdenum in aqueous sulphuric acid have also been investigated,[55] and in this case it is suggested that the greater oxidising activity of sulphur dioxide as gas, or in high acid concentrations, may be explained by its existence as the hydrate, SO_2,H_2O.[56] Auto-oxidation of aqueous sulphurous acid, forming sulphuric acid and sulphur, is found to proceed, though slowly, at 100° and to be auto-catalytic in its earlier stages; it is completely suppressed in 2*N*-hydrochloric acid.[57]

Action of a silent electrical discharge upon a current of sulphur dioxide and oxygen has yielded oxidation products as high as that represented by $SO_3,2SO_4$, whence it seems possible that Berthelot's "sulphur heptoxide" may have been a mixture of the trioxide and tetroxide.[58]

Several physical properties of sulphur trioxide have been redetermined: m. p. 16·85° ± 0·02°; b. p. 44·52°/760 mm.; $d^{20°}$ 1·9255; critical pressure, 83·8 atms.; critical temperature, 218·3°; critical density, 0·633. The observations are held to indicate that β-SO_3 is probably an indefinite hydration compound and not a simple polymeric modification of α-SO_3.[59]

Sodium thiosulphate and cupric nitrate in cold aqueous solution produce disodium tricuprous thiosulphate, $3Cu_2S_2O_3,2Na_2S_2O_3,6H_2O$, crystallising in yellow needles which, when well washed and air-dried, are permanent. The primary reaction of formation is simply $2Cu(NO_3)_2 + 3Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_4O_6 + 4NaNO_3$. Copper sulphate and cupric chloride give similar results, but in the former case the yellow salt is contaminated with the salt

$$3Cu_2SO_4,2Na_2SO_4,6H_2O$$

in solid solution, and in the latter case it soon changes to a white salt, $Cu_2S_2O_3,Na_2S_2O_3,H_2O$, containing $Cu_2Cl_2,2NaCl,H_2O$ in solid solution. Using excess of thiosulphate in presence of a mineral acid at 100°, the double salt is decomposed to form cuprous sulphide, $3Cu_2S_2O_3,2Na_2S_2O_3,6H_2O \longrightarrow 3Cu_2S + 2Na_2SO_4 + H_2SO_4 + 2SO_2 + 2S + 5H_2O$, this precipitation of copper being quantitative

[53] S. R. Carter and J. A. V. Butler, *T.*, 1923, **123**, 2370.

[54] *Idem, ibid.*, p. 2370.

[55] W. Wardlaw and N. D. Sylvester, *ibid.*, p. 969. [56] *Idem, ibid.*, p. 3417.

[57] F. Foerster, F. Lange, O. Drossbach, and W. Seidel, *Z. anorg. Chem.*, 1923, **128**, 245; *A.*, ii, 853.

[58] F. Meyer, G. Bailleul, and G. Henkel, *Ber.*, 1922, **55**, [*B*], 2923; *A.*, 1922, ii, 843.

[59] A. Berthoud, *J. Chim. Phys.*, 1923, **20**, 77; *A.*, ii, 315.

if sulphuric acid or nitric acid in a concentration less than $N/2$ is used. Under such conditions also, a reaction occurs between sodium tetrathionate, sodium thiosulphate, and the mineral acid whereby pentathionic acid is produced:

$$Na_2S_4O_6 + Na_2S_2O_3 + 4H\bar{A} \longrightarrow H_2S_5O_6 + 4Na\bar{A} + H_2O + SO_2.$$

To account for the relatively great stability of pentathionic acid in presence of concentrated mineral acids, in sharp contrast with its instability in alkaline solution, it is suggested that whilst the molecule $H_2S_5O_6$ is stable, the anions HS_5O_6' and S_5O_6'' are very unstable.[60]

Pure selenium trioxide has been obtained by the action of dry ozone on selenium in presence of selenium oxychloride as a solvent. After washing with carbon tetrachloride and ether, it is a pale-yellow, amorphous solid, d 3·6, decomposing at 120° to form selenium dioxide and oxygen; its molecular weight in phosphorus oxychloride solution corresponds with the simple formula SeO_3. A white, crystalline sublimate observed during the preparation, possibly an allotropic modification, was not obtained in sufficient quantity for investigation. Selenium trioxide is soluble in alcohol, but insoluble in ether, benzene, chloroform, or carbon tetrachloride. It reacts with water and alkalis, forming selenic acid and selenates, dissolves in selenic acid, and combines directly with dry hydrogen chloride to form chloroselenic acid, the analogue of chlorosulphonic acid. Chloroselenic acid is a nearly colourless liquid, f. p. — 46°, d 2·26; it fumes in air, evolving hydrogen chloride: it is insoluble in ether, benzene, chloroform, or carbon tetrachloride, dissolves unchanged in selenium oxychloride, and is dissolved and decomposed by water or alcohol. Its molecular weight in phosphorus oxychloride solution corresponds to the double formula $(HClSeO_3)_2$.[61]

The solubility of a number of anhydrous metallic chlorides in selenium oxychloride has been determined and the following double compounds have been isolated: $TiCl_4,2SeOCl_2$; $SnCl_4,2SeOCl_2$; $SbCl_5,2SeOCl_2$; $FeCl_3,2SeOCl_2$; $KCl,SeOCl_2$; $RbCl,SeOCl_2$; $CaCl_2,3SeOCl_2$; $MgCl_2,3SeOCl_2$.[62]

Selenium nitride may best be obtained by interaction between selenium tetrachloride or tetrabromide and liquid ammonia; it is an amorphous, orange-coloured powder, exploding with certainty at 160° and more sensitive than mercury fulminate to shock; it probably has a cyclic structure and the formula Se_4N_4.[63]

[60] H. Bassett and R. G. Durrant, *T.*, 1923, **123**, 1279.
[61] R. R. le G. Worsley and H. B. Baker, *ibid.*, 1923, **123**, 2870.
[62] C. R. Wise, *J. Amer. Chem. Soc.*, 1923, **45**, 1233; *A.*, ii, 484.
[63] W. Strecker and L. Claus, *Ber.*, 1923, **56**, [*B*], 362; *A.*, ii, 152.

Some new series of phosphotungstates are described [64] including the simple series $3M_2O,P_2O_5,6WO_3,aq.$, of which the sodium, potassium, and ammonium salts have been prepared in the pure state.[65] Investigation of the reaction between incandescent tungsten filaments and naphthalene vapour indicates the existence of two carbides, WC and W_2C.[66]

The system chromium trioxide–nitric acid–water is simple: chromium trioxide is the only solid phase and has a minimum solubility in liquids containing about 70—90 per cent. of nitric acid.[67]

Group VII.

It is reported that pure chlorine is activated by the silent discharge, by ultra-violet light or thermally, and then reacts with ozone, forming chlorine monoxide; with sulphur, forming the monochloride; with tellurium to form the dichloride; and with benzene in the dark to form the hexachloride. Active chlorine is unstable above 50° and its formation is attended by a decrease in volume attributed to formation of complex molecules.[68]

Precise gravimetric determinations have been made of the composition of constant-boiling mixtures of hydrogen chloride and water.[69] A number of new chlorites are described, including those of hydrazine, $N_2H_4,HClO_2$, rubidium, and cæsium; mercury, $HgClO_2$ and $Hg(ClO_2)_2$; zinc and cadmium, $Zn(ClO_2)_2,2H_2O$; $Cd(ClO_2)_2,2H_2O$; and copper, $Cu(ClO_2)_2$.[70] Determinations have been made of the solubility of the perchlorates of a number of metals (Li, Na, K, Rb, Cs, NH_4, Mg, Ca, Sr, Ba) in water, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, *iso*butyl alcohol, acetone, ethyl acetate, and ethyl ether.[71]

The perchlorates of the alkali metals (except lithium), silver, and thallium are found to exist in enantiotropic forms, the transition points being as follows: $NaClO_4$, 308°; $KClO_4$, 300°; $RbClO_4$, 279°; $CsClO_4$, 219°; NH_4ClO_4, 240°; $AgClO_4$, 157°; $TlClO_4$, 266°.[72]

Chlorine tetroxide, $(ClO_4)_x$ (where x probably = 2), has been

[64] F. Kehrmann and R. Mellet, *Helv. Chim. Acta*, 1922, **5**, 942; *A.*, ii, 77.

[65] *Idem*, *ibid.*, 1923, **6**, 443; *A.*, ii, 497.

[66] Mary R. Andrews, *J. Physical Chem.*, 1923, **27**, 270; *A.*, ii, 327.

[67] S. A. Mumford and L. F. Gilbert, *T.*, 1923, **123**, 471.

[68] Y. Venkataramaiah, *J. Physical Chem.*, 1923, **27**, 74; *A.*, ii, 149.

[69] C. W. Foulk and M. Hollingsworth, *J. Amer. Chem. Soc.*, 1923, **45**, 1220; *A.*, ii, 482.

[70] G. R. Levi, *Gazzetta*, 1923, **53**, i, 105, 200, 245; *A.*, ii, 406, 421, 492. *Atti R. Accad. Lincei*, 1923, [v], **32**, i, 165, 623; *A.*, ii, 421, 767.

[71] H. H. Willard and G. F. Smith, *J. Amer. Chem. Soc.*, 1923, **45**, 286; *A.*, ii, 239.

[72] D. Vorländer and E. Kaascht, *Ber.*, 1923, **56**, [*B*], 1157; *A.*, ii, 487.

prepared in 0·1*N*-anhydrous ethereal solution by the action of iodine upon silver perchlorate; small amounts of a labile iodine compound, assumed to be iodine tetroxide, are simultaneously formed, but readily decompose into iodine and oxygen. Chlorine tetroxide is stable in ethereal solution and does not volatilise with ether.[73]

Manganese prepared electrolytically has *d* 7·034—7·080; it has no action on cold water and very little on steam at 500°; it burns brilliantly in oxygen or chlorine and when heated in a blowpipe flame forms a nitride decomposable by water with formation of ammonia. Manganese reacts with concentrated sulphuric acid to form manganous sulphate and sulphur dioxide; and with nitric acid in a manner dependent on the concentration of the acid; 10 per cent. acid gives chiefly hydrogen, and 100 per cent. acid principally nitrogen peroxide as the gaseous product.[74]

A dark red solution of a higher chloride of manganese, similar to Scheele's solution obtained by dissolving manganese dioxide in cold hydrochloric acid, has been prepared by anodic oxidation of 3*M*-manganous chloride solution, and is shown to contain, in addition to this salt, only the tetrachloride, $MnCl_4$.[75]

Group VIII.

Preliminary experiments show that a hitherto unrecognised factor is operative in the corrosion of iron: [76] the rate of solution of oxygen in water and the rate of corrosion both vary with the humidity of the surrounding air. Apparently, the relatively vigorous convection currents set up by the surface cooling consequent on evaporation into dry air materially facilitate the dissolution of oxygen.

Investigation of the system ammonium chloride–ferric chloride–water at 25° and 60° confirms the existence of a compound $NH_4Cl,FeCl_3$ described by Mohr [77] and discloses a solid, $NH_4Cl,4FeCl_3,6H_2O$, in equilibrium with certain solutions at 60°, but shows that the supposed compound $2NH_4Cl,FeCl_3,H_2O$ is really a series of solid solutions within narrow limits approximating to this composition, and affords no evidence for Mohr's reported compound, $NH_4Cl,2FeCl_3,4H_2O$.[78]

In the system ferric oxide–phosphoric acid–water at 25°, the

[73] M. Gomberg, *J. Amer. Chem. Soc.*, 1923, **45**, 398; *A.*, ii, 235.
[74] A. N. Campbell, *T.*, 1923, **123**. 2323.
[75] *Idem, ibid.*, p. 892.
[76] J. A. Newton Friend, *ibid.*, 1923, **123**, 2996.
[77] Mohr, *Z. physikal. Chem.*, 1898, **27**, 193.
[78] F. W. J. Clendinnen, *T.*, 1923, **123**, 1338.

solid phase in equilibrium with low acid concentrations is Fe_2O_3,P_2O_5,xH_2O, which adsorbs acid and at higher acid concentrations changes to a true compound, $Fe_2O_3,P_2O_5,5H_2O$, probably a ferric ferriphosphate, $Fe[Fe(PO_4)_2],5H_2O$. At 70°, these phases still exist, also the $Fe_2O_3,2P_2O_5,8H_2O$ and $Fe_2O_3,3P_2O_5,6H_2O$ already known, and a new compound crystallising in small, pink, hexagonal plates, probably $Fe_2O_3,3P_2O_5,10H_2O$.[79]

Anhydrous cobalt iodide at 570—575° in a vacuum suffers some decomposition and in part sublimes, forming black crystals of the ordinary iodide and a small quantity of a yellow powder which is a second form of the salt, termed β-cobalt iodide. This is extremely hygroscopic and yields a yellow, aqueous solution from which chloroform extracts iodine; this leaves the solution colourless, but it reverts to the usual rose colour of the iodide solutions on warming or concentration.[80]

Three unstable bismuthyl cobaltinitrites and a stable, yellow cadmium cobaltinitrite, $Cd_3[Co(NO_2)_6]_2$, have been prepared;[81] and triple nitrites of cobalt and lead with potassium, rubidium, ammonium, and thallium are described, the formation of the first-named constituting a very sensitive test for potassium.[82]

The action of aqueous alkali and hypochlorite on a nickel salt produces simultaneously nickel dioxide and sesquioxide. Nickel dioxide decomposes directly to nickelous oxide, $Ni(OH)_2$, whilst under these conditions the sesquioxide is not directly oxidisable to the dioxide; there is therefore a limit to the oxygen content of the precipitate.[83]

By warming an aqueous solution of potassium chloroiridiate with excess of hydrazine hydrochloride a reddish-brown solution is obtained containing the complex acid $[Ir(N_2H_5)Cl_5]H$, of which crystalline cæsium and platinitetrammine salts have been prepared.[84]

Lithium platinocyanide, variously described in the literature, is when pure a yellowish-green salt, but its colour is much changed by traces of other alkalis; it forms several hydrates, among which those with $4H_2O$ and $5H_2O$ can be characterised from the dehydration curves. Lithium potassium platinocyanide, $LiKPt(CN)_4,2H_2O$, forms ruby-red crystals with a characteristic blue shimmer, and on dehydration gives a yellow solid readily rehydrating on exposure.[85]

[79] S. R. Carter and N. H. Hartshorne, *T.*, 1923, **123**, 2223.
[80] E. Birk and W. Biltz, *Z. anorg. Chem.*, 1923, **128**, 45; *A.*, ii, 866.
[81] S. C. Ogburn, *J. Amer. Chem. Soc.*, 1923, **45**, 641; *A.*, ii, 328.
[82] V. Cuttica, *Gazzetta*, 1923, **53**, i, 185; *A.*, ii, 497.
[83] O. R. Howell, *T.*, 1923, **123**, 1772.
[84] L. Tschugaev, *Ber.*, 1923, **56**, [*B*], 2067; *A.*, ii, 774.
[85] H. Terry and V. G. Jolly, *T.*, 1923, **123**, 2217.

The preparation of a number of new platinum ammine compounds is reported,[86] and depolymerisation of certain inorganic bicomplex platinum compounds has been observed.[87]

H. V. A. Briscoe.

[86] L. A. Tschugaev *et al.*, *J. Russ. Phys. Chem. Soc.*, 1920, **51**, 193; *A.*, ii, 499.

[87] L. A. Tschugaev and N. K. Pschenicyn, *ibid.*, 1920, **52**, 47; *A.*, 1922, ii, 856.

ORGANIC CHEMISTRY.

Part I.—Aliphatic Division.

Researches devoted to problems falling within this division have greatly increased both in volume and importance during the past year. Some of these have had, perforce, to receive the briefest mention and much that is of interest is unavoidably omitted. This is to be regretted, and it is hoped that authors will appreciate that only limitations of space have imposed this curtailment. The practice recently instituted of holding over for biennial review the problems of optical activity has again been observed, inasmuch as a period of two years was covered in the Report of 1922.

Hydrocarbons.

Current theories as to the genesis of petroleum are either the result of speculation or of isolated experiments of a limited range such as that performed by Engler on the pyrogenic decomposition of fish blubber. A new survey of the factors governing the organic transformation of vegetable and animal remains into hydrocarbons or coal is of general interest [1] and it is illuminating to discover that analyses of a large number of samples of mineral oils and asphalts from many quarters of the world reveal the presence of appreciable quantities of nickel either in solution or in colloidal suspension.[2] Sabatier and Senderens have advanced the theory that catalytic hydrogenation may be a factor in the production of petroleum, and this observation lends support to their view.

Catalytic hydrogenation has been studied from the point of view of steric hindrance by selecting olefines containing side chains differently situated with respect to the double linking.[3] The theory of steric retardation holds for this reaction, although the additive combination with bromine is at variance with the rule. The reduction of carbon monoxide to methane occurs in the presence of iron as catalyst,[4] and provided that the pressure is increased to 40 atmospheres the main reaction at 400° is the formation of equal

[1] R. d'Andrimont, *J. Inst. Petr. Tech.*, 1923, **9**, 287; *A.*, i, 993.
[2] W. Ramsay, *J. Soc. Chem. Ind.*, 1923, **42**, 287; *A.*, i, 737.
[3] G. Vavon and S. Kleiner, *Compt. rend.*, 1923, **177**, 401; *A.*, i, 891.
[4] F. Fischer and H. Tropsch, *Brennstoff-Chem.*, 1923, **4**, 193; *A.*, i, 737.

volumes of methane and carbon dioxide from mixed gases containing equal volumes of carbon monoxide and hydrogen. Catalysis of the reaction leading to the formation of olefines and cyclenes by the dehydration of alcohols is more conveniently and rapidly conducted with the aid of sulphuric acid than with dry catalysts such as aluminium sulphate. This inference is drawn by Senderens [5] in a review of his work on this subject which shows that, whilst theoretically the dry method is more efficient, in practice the wet method is more advantageously operated. The reaction does not require the use of a large proportion of acid except for the purpose of attaining a mixture of such boiling point as to allow the catalytic action to proceed.

It is noteworthy that for the absorption of ethylene from gaseous mixtures chlorosulphonic acid [6] is more effective than sulphuric acid even with rapid currents of gas. Waste gases having a low content of ethylene can thus be utilised to prepare ethyl chlorosulphonate, which yields ethyl chloride or ethyl alcohol when treated with hydrochloric acid or water, respectively. On the other hand, the speed of fixation of ethylene with concentrated sulphuric acid is accelerated by using cuprous oxide as catalyst. An extended inquiry into the mechanism of the Wurtz-Fittig synthesis [7] leads to a conception of the transitory existence of a free radical as the primary change: $R{\cdot}Hal + Na \longrightarrow R{\cdot} + NaHal$. In the second phase, the radical may unite with sodium to give the sodium alkyl, RNa, or polymerise to the hydrocarbon R·R. If the conditions are such that a hydrogen atom is readily displaced, the radical is transformed into R — H or R + H. The third phase is represented by the union of the sodium alkyl with alkyl halide, or the loss or gain of hydrogen by the radical may occur again. The last is the main change in the aliphatic series from ethyl upwards to cetyl, but with methyl the radicals combine to give ethane. Complications due to solvent may arise, for example, sodium ethyl reacts with ether in accordance with the equation $EtOEt + NaEt \longrightarrow NaOEt + C_2H_4 + C_2H_6$. The formation of a new lead alkyl is reported,[8] namely, Pb_2Et_6. This is a heavy, yellow oil, unstable in air, prepared by electrolysis of lead triethyl hydroxide in ethyl alcohol.

Contradictory evidence has in the past been furnished as to the

[5] *Ann. Chim.*, 1922, [ix], **18**, 117; *A.*, i, 9; *Compt. rend.*, 1923, **176**, 813; *A.*, i, 432.

[6] W. Traube and R. Justh, *Brennstoff-Chem.*, 1923, **4**, 150; *A.*, i, 641; A. Damiens, *Compt. rend.*, 1922, **175**, 585; *A.*, 1922, i, 1105.

[7] H. A. Schlubach and E. C. Goes, *Ber.*, 1922, **55**, [*B*], 2889; *A.*, 1922, i, 1204.

[8] T. Midgley, jun., C. A. Hochwalt, and G. Calingaert, *J. Amer. Chem. Soc.*, 1923, **45**, 1821; *A.*, i, 906.

mode of attachment of hydrogen halides to isoprene, and a new investigation [9] makes clear the grounds of previous differences. Hydrogen bromide combines with ice-cold isoprene with the initial formation of the tertiary bromide, involving addition at the 1 : 2 positions :

$$CH_2{:}CMe{\cdot}CH{:}CH_2 \longrightarrow CMe_2Br{\cdot}CH{:}CH_2.$$

If the tertiary bromide is kept a few hours before distillation and especially if free hydrogen bromide is present, it undergoes isomeric change into the primary bromide, $CMe_2{:}CH{\cdot}CH_2Br$, a product representing 1 : 4 addition of the hydrogen halide in accordance with Thiele's rule. This last compound has been carefully characterised, and is found to be unusually unstable towards water with the formation of the tertiary alcohol, a change which is reversible,

$$CMe_2{:}CH{\cdot}CH_2Br + H_2O \rightleftharpoons HO{\cdot}CMe_2{\cdot}CH{:}CH_2 + HBr.$$

An observation of fundamental importance is communicated showing that the additive union of ethylene and bromine is almost suspended if the gaseous reagents are brought together in a vessel coated internally with paraffin wax, whilst the reaction is accelerated beyond the rate at which it occurs on glass surfaces if the wax coating is replaced by one of stearic acid.[10] The inference is drawn that the reactant molecules require activation with a polar catalyst as a preliminary to reaction. A glass surface supplies this requirement, and particularly so does a polar substance such as stearic acid and also, to a less extent than either of these, cetyl alcohol. The comparative effect of the surfaces in promoting the reaction is indicated roughly by the ratios 30, 20, 10, 1, respectively, for stearic acid, glass, cetyl alcohol, and paraffin wax, and if it were possible to avoid crevices in the wax allowing access to the glass vessel it is suggested that the reaction would be entirely suppressed. The phenomenon is thus comparable with that observed in numerous cases where reactions between thoroughly dried gases are entirely suspended. This view of molecular activation coupled with the kinetic theory is held to be sufficient to explain all the phenomena of chemical reactivity without recourse to other hypotheses such as the "radiation theory."

Lowry's conception [11] of an activated unsaturated molecule is to regard the double bond as equivalent to one covalency and one

[9] L. Claisen, F. Kremers, F. Roth, and E. Tietze, *J. pr. Chem.*, 1922, [ii], **105**, 65, 288; *A.*, i, 1050.

[10] R. G. W. Norrish, *T.*, 1923, **123**, 3006.

[11] T. M. Lowry, *ibid.*, p. 822; compare also A. M. Berkenheim, *J. Russ. Chem. Soc.*, 1917, **49**, ii, 1; *A.*, i, 525.

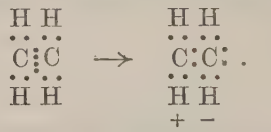
electrovalency, so that the resting state for ethylene acquires the polar form indicated below :

$$CH_2{=}CH_2 \longrightarrow \overset{+}{C}H_2{-}\overset{-}{C}H_2 \quad . \quad . \quad . \quad . \quad . \quad (A)$$

The carbon atom which receives an electron assumes a negative character and the contiguous carbon deprived of an electron becomes positive. Chemical union of ethylene and bromine may thus be formulated,

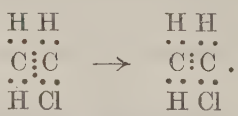
$$\overset{+}{C}H_2{-}\overset{-}{C}H_2 + \overset{-}{Br} + \overset{+}{Br} \longrightarrow CH_2Br{-}CH_2Br$$

The idea is an alternative mode of expression of the electronic theory of valency, and in effect the result of equation A may be shown :



(B)

In B, the two carbon atoms are linked only by two shared electrons constituting a co-valency, whilst the negative carbon atom has retained its own fourth electron and gained one in addition from the positive carbon atom. Kermack and Robinson (see last year's Report, p. 63) do not apply their theory to the simple case of ethylene and consider that the linking here is purely one of co-valency. Should the symmetrical nature of ethylene be invaded as by substitution in the case of vinyl halide, it is suggested by these authors that the polar conditions are set up, and their explanation of the transfer of electrons differs from that attributed by Lowry in the sense that even in this case a simple co-valency bond is not necessarily established,

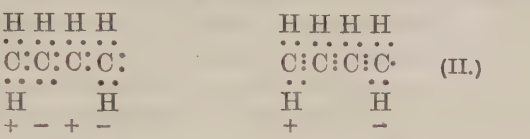


Acetylene is regarded also by Lowry as a polar compound having a mixed treble bond, and its combination with water is shown in the formation of acetaldehyde :

$$\overset{-}{C}H{\equiv}\overset{+}{C}H + HOH \longrightarrow CH_2{=}CH{\cdot}OH \longrightarrow CH_3{-}\overset{+}{C}H{-}\overset{-}{O}$$

The wide difference between the reactivity of single and double bonds is thus attributed to the development of electrovalency in the latter. The special reactivity of the Grignard reagents is attributed to their polar character, $\overset{-}{I}{\cdots}\overset{++}{Mg}{\cdots}\overset{-}{C}H_3$, in that they contain a

methyl-ion, and in this connexion it is now on record [12] that magnesium alkyl halides function as electrolytes. The active phase of butadiene is represented as $\overset{+}{C}H_2—\underset{-}{C}H—\overset{+}{C}H—\underset{-}{C}H_2$, an expression which is equivalent to (I) as compared with Kermack and Robinson's formulation (II), and it is claimed by Lowry that, in his new



formula, whilst the main polarity and unsaturation are at the ends of the chain, the alternate polarities and unsaturation exist also in the intermediate atoms, thus providing an explanation of the attachment of 1 : 2- as well as 1 : 4-addenda. It would appear, however, that whilst the Lowry formula definitely excludes such a phase as that indicated by Kermack and Robinson's representation, the latter does not exclude the possibility of change into another phase such as is suggested by Lowry, and thus preserves greater elasticity as a mode of expression.

The general application of Thiele's theory has been defended against criticisms to which it has recently been subjected. It is pointed out,[13] for example, that in the case of muconic acid, the free partial valencies occur, not in the 1 : 4-, but in the 1 : 6-positions,

$$O{=}C(OH){\frown}CH{=}CH{\frown}CH{=}CH{\frown}C(OH){=}O,$$

and the attachment of hydrogen occurs first on the oxygen, followed by rearrangement. Since bromine does not combine directly with oxygen, this 1 : 6 addition is not possible when bromine and muconic acid interact.

A suggestion is made that the reactions used in earlier attempts to investigate the constitution of caoutchouc have been too drastic, and a new series of experiments in which hydrogen peroxide is employed as oxidising medium leads to the proposal of a new structural formula.[14]

Alcohols and Derivatives.

A convenient procedure for the purification of methyl alcohol is devised [15] involving the elimination of acetone by the agency of sodium hypochlorite, which converts the acetone into chloroform,

[12] N. V. Kondyrev, *J. Russ. Chem. Soc.*, 1920, **52**, 17; *A.*, 1922, i, 1128.
[13] F. Allsop and J. Kenner, *T.*, 1923, **123**, 2296.
[14] M. C. Boswell, *Trans. Roy. Soc. Canada*, 1922, **16**, iii, 27; *A.*, i, 350.
[15] R. C. Menzies, *T.*, 1922, **121**, 2787; H. H. Bates, J. M. Mullaly, and H. Hartley, *T.*, 1923, **123**, 401.

and this latter product is easily eliminated by fractional distillation. An analogous method, suitable for small concentrations of acetone, and more especially serviceable for laboratory use, is provided by utilising sodium hypoiodite, and the authors have examined the degree of accuracy attainable by the usual method of estimating acetone in presence of methyl alcohol. The drying of methyl alcohol by magnesium and the determination of the initial hydration have been the subject of quantitative study,[16] so that it is now possible by measuring the hydrogen evolved at room temperature and reference to a published graph to determine the progress of the drying operation. An apparatus is also devised by means of which ethyl alcohol of 99·5 per cent. concentration may rapidly be prepared with the agency of calcium chloride, and an alternative form is suggested for manipulating the use of lime for the drying of alcohol.[17] Catalytic reduction of acetaldehyde or paracetaldehyde occurs at 200° when their vapours mixed with hydrogen are passed over activators consisting of finely divided copper and water-glass or of colloidal silicic acid and pumice. This enables acetylene to be employed as a source of ethyl alcohol.

Considerable interest is manifested in the mechanism which leads to the conversion of alcohols into ethers or hydrocarbons, and in addition to the discussion introduced in the section on hydrocarbons, other results of value are contributed. A study of the conditions essential to the formation of a high yield of ethers shows that these are dependent on an understanding of the properties of binary mixtures of alcohol and water and the ternary mixtures of alcohol, ether, and water. From a knowledge of the boiling points of these mixtures and the composition of the vapour phase in each case, the preparation of ethers may be effected with yields of about 90 per cent. by simple distillation of the alcohols with sulphuric acid, and success has been attained on these lines with many alcohols.[18] The usual equations

$$(a)\ \mathrm{EtOH} + \mathrm{H_2SO_4} = \mathrm{EtHSO_4} + \mathrm{H_2O}$$
$$(b)\ \mathrm{EtHSO_4} + \mathrm{EtOH} = \mathrm{H_2SO_4} + \mathrm{Et_2O}$$

which purport to express the formation of ethyl ether are inaccurate, since they fail to take account of the existence and function of the various hydrates of sulphuric acid which participate.[19] In presence of alcohol, the penta-, tetra-, tri-, and di-hydrates correspond with

[16] N. Bjerrum and L. Zechmeister, *Ber.*, 1923, **56**, [*B*], 894; *A.*, i, 529.

[17] W. A. Noyes, *J. Amer. Chem. Soc.*, 1923, **45**, 857; *A.*, i, 433; Badische Anilin- & Soda-Fabrik, D.R.-P. 362537; Brit. Pat. 175238; from *Chem. Zentr.*, 1923, ii, 478; *A.*, i, 739.

[18] J. Popelier, *Bull. Soc. chim. Belg.*, 1923, **32**, 179; *A.*, i, 532.

[19] J. B. Senderens, *Compt. rend.*, 1923, **177**, 15; *A.*, i, 742.

the temperatures 110—121°, 121—130°, 130—145°, and 145—162°, respectively. Ethylene tends to be formed to the exclusion of ether at 145°. No ethylene is produced at 130°, but the effective hydrate here is the tetrahydrate, which is surpassed by the trihydrate in etherifying properties. Consequently, the optimum temperature for the production of ethyl ether is 136—138°, which is higher than that usually employed by manufacturers. The production of methyl ether avoids the complication of ethylene formation and it is possible here to use the still more effective dihydrate and employ temperatures up to 160—165°.

The dehydrating action of phosphoric oxide [20] on alcohol vapour or ether vapour is partly catalytic and partly dependent on the formation of unstable additive products. At the ordinary temperature alcohol gives, with phosphoric oxide, metaphosphoric acid and the esters $Et_2H_2P_2O_7$, EtH_2PO_4, Et_2HPO_4, and Et_3PO_4, and also dehydrates the second and third of these esters, giving a mixture of ethyl meta- and pyro-phosphates.

Evidence of the existence of an oxonium compound [21] in the vapour phase is adduced in the case of methyl ether–hydrogen chloride. Its formation is attributed to induced polarity in the ether molecule caused by the polar molecule of hydrogen chloride. The similarity between this compound and ammonium chloride has been commented on.

Few criteria of purity have been recorded with such a high degree of accuracy as those which are now available for a considerable number of aliphatic alcohols and ketones.[22] The boiling points have been determined by the use of a thermo-element, and other data include the measurement of refractive index and density. Geometric isomerides of the crystalline dimethylhexenediol (I) have been prepared.[23] Conversion of both isomerides into the cyclic oxide (II)

(I.) $\begin{matrix} CH\cdot CMe_2\cdot OH \\ \| \\ CH\cdot CMe_2\cdot OH \end{matrix}$ (II.) $\begin{matrix} CH\cdot CMe_2 \\ \| \\ CH\cdot CMe_2 \end{matrix}\!\!>\!O$

occurs with iodine or by heating with sulphuric acid or potassium hydrogen sulphate.

In a series of papers by R. Delaby [24] a general procedure is described for obtaining alkylvinylcarbinols of the general formula

$$CH_2{:}CH\cdot CHR\cdot OH$$

[20] D. Balareff, *J. pr. Chem.*, 1922, [ii], 368; *A.*, i, 287.

[21] O. Maass and D. M. Morrison, *J. Amer. Chem. Soc.*, 1923, **45**, 1675; *A.*, i, 892.

[22] R. F. Brunel, *ibid.*, p. 1334; *A.*, i, 646.

[23] Jul. Salkind, *Ber.*, 1923, **56**, [*B*], 187; *A.*, i, 176.

[24] *Bull. Soc. chim.*, 1923, [iv], **33**, 602, 753; *A.*, i, 741; *Compt. rend.*, 1922, **175**, 967, 1152; *A.*, i, 84, 85; *Compt. rend.*, 1923, **176**, 1326, 1898; *A.*, i, 646.

by the action of a Grignard reagent on acraldehyde. The substances are of interest in that they lead to the preparation of substituted glycerols by transformation of their bromides into diacetates, followed by hydrolysis of the latter. Thus a number of alkyl glycerols, $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CHR{\cdot}OH$, have been made available, and the experimental details leading to these results are worthy of notice.

Aldehydes and Ketones.

Systematic inquiry into sources of formaldehyde other than that of methyl alcohol has been vigorously prosecuted since the marked advances in this direction were reported last year. T. S. Wheeler and E. W. Blair [25] have turned their attention from the catalysis of heated mixtures of ethylene and oxygen to a similar study of methane and coal gas, united with oxygen or ozone, but there are few noteworthy results which register improvement on earlier records, although the interim reports are promising. A parallel investigation [26] is also in progress in which methane is oxidised with the oxides of sulphur or nitrogen with or without silica as catalyst. With sulphur trioxide in presence of a large excess of methane at 595° a small quantity of methane oxidised entirely to formaldehyde.

Synthetic acetaldehyde being now available from acetylene, it is obviously an economic project to explore all the possible commercial uses of this reagent. An unexpected direction [27] in which it has found application is in the production of its lower homologue, formaldehyde, which is obtained in a yield of 50 per cent. by passing one kilogram of acetaldehyde mixed with a cubic metre of air over a coil of copper wire netting. Of similar interest is the production of crotonaldehyde by circulation of acetaldehyde at 300° over a selection of catalysts. Meanwhile, the standard process for the preparation of formaldehyde from methyl alcohol has been notably improved by using as catalyst copper gauze disks packed perpendicularly to the axis of the oxidation chamber instead of the more usual copper spirals. Not only is it permissible to utilise crude methyl alcohol of considerable acetone content, but the advantage of yield is so striking that the modification cannot be ignored, since the author [28] claims to have increased the efficiency from 40 to 70 per cent. Two independent attempts to repeat the photo-

[25] *J. Soc. Chem. Ind.*, 1922, **41**, 331; 1923, **42**, 81, 87, 260, 343; *A.*, 1922, i, 1105; 1923, i, 285, 752, 997.

[26] E. Berl and H. Fischer, *Z. angew. Chem.*, 1923, **36**, 297; *A.*, i, 641.

[27] Consortium für Elektrochemische Industrie, Brit. Pat. 178842; D.R.-P. 349915; from *Chem. Zentr.*, 1922, iv, 43; *A.*, 1922, i, 1115; 1923, i, 752.

[28] P. Bobrov, *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 130; *A.*, i, 300.

chemical formation of formaldehyde from carbon dioxide which has previously been reported have met with failure.[29] A comprehensive survey of the properties of formaldehyde, with particular reference to the electrolysis and catalytic decomposition of its solution, furnishes evidence [30] of the existence and amphoteric nature of the hydrate, $CH_2(OH)_2$, and these observations are extended to other substances containing the carbonyl group, such as ketones, carboxylic acids, and also carbon monoxide. A new polymeride of formaldehyde, ϵ-polyoxymethylene, has been prepared from α-trioxymethylene by repeated sublimation, and this new substance does not respond to acetylation and therefore contains no hydroxyl groups, nor does it reduce ammoniacal silver oxide.[31] Paraformaldehyde gives rise to a 22 per cent. yield of glycollic acid along with methyl formate on heating at 115° in an autoclave.

Improvements in the laboratory preparation of acetaldehyde were recorded in the last Report, and these are now supplemented by E. Wertheim,[32] who recommends that the oxidation of ethyl alcohol should be conducted with a mixture containing nitric acid, sulphuric acid, and sodium dichromate, and that a stream of carbon dioxide should be passed through the reaction mixture in order to carry over the product and prevent its further oxidation. For the preparation of acetal, the use of metallic halides is again suggested and these are said to act as true catalysts. The catalytic synthesis of acetals from acetylene is announced as a general procedure and furnishes moderately good results. Thus dimethylacetal and diethylacetal are prepared by passing acetylene into the appropriate alcohol in presence of concentrated sulphuric acid and mercuric sulphate.[33] Halogenation of the acetals provides a route to a variety of useful reagents; for example, among the products of chlorination of dimethylacetal are monochloro- and *s*-dichlorodimethyl ether, whilst the more highly halogenated ethers also are obtained on bromination. On chlorinating diethylacetal, chloral is formed. A useful variation [34] of the general procedure for preparing the acetals of ketones is described in which ethyl orthoformate in presence of sulphuric acid is employed, and a number of aliphatic ketones have responded to this reagent.

A welcome addition to the available methods for the synthesis

[29] Emil Baur and A. Rebmann, *Helv. Chim. Acta*, 1922, **5**, 828; *A.*, i, 91. H. A. Spoehr, *J. Amer. Chem. Soc.*, 1923, **45**, 1184; *A.*, ii, 452.

[30] *Z. angew. Chem.*, 1922, **35**, 689, 698; *A.*, i, 90.

[31] D. L. Hammick and A. R. Boeree, *T.*, 1922, **121**, 2738; 1923, **123**, 2881.

[32] *J. Amer. Chem. Soc.*, 1922, **44**, 2658; *A.*, i, 14.

[33] J. S. Reichert, J. H. Bailey, and J. A. Nieuwland, *ibid.*, 1923, **45**, 1552; *A.*, i, 753.

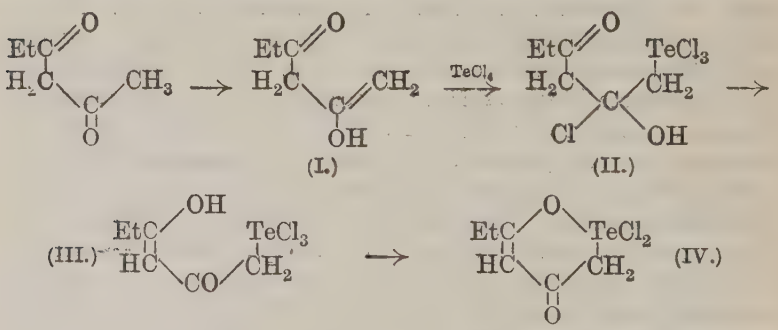
[34] V. V. Evlampiev, *J. Russ. Phys. Chem. Soc.*, 1923, **54**, 462; *A.*, i, 1061.

of aldehydes and ketones is reported as the outcome of the observation that alkyl hypochlorites, which have long been known to be unstable compounds, decompose either on heating or in bright sunlight,[35] and ketones or aldehydes are formed along with hydrogen chloride or alkyl chloride. This valuable observation renders it possible to prepare aldehydes and ketones from alcohols without recourse to the more usual oxidation processes. In general terms, the reactions may be expressed as :

$$\begin{aligned} R{\cdot}CH_2{\cdot}OH &\longrightarrow R{\cdot}CH_2{\cdot}OCl \longrightarrow R{\cdot}CHO + HCl. \\ R_2CH{\cdot}OH &\longrightarrow R_2CH{\cdot}OCl \longrightarrow R_2CO + HCl. \\ R_3C{\cdot}OH &\longrightarrow R_3{\cdot}COCl \longrightarrow R_2CO + RCl. \end{aligned}$$

Since the hypochlorites are available in quantitative yield, by admitting chlorine to a well-cooled mixture of alcohol and alkali with the exclusion of light, it is apparent that this reaction will find many applications.

The behaviour of diketones in contact with tetrachlorides of tellurium and selenium [36] continues to furnish interesting examples of co-ordination. The following compounds of the tellurium type are given showing the behaviour of acetylpropionylmethane.



The formulæ I, II, and III represent intermediate phases; the product isolated is indicated by IV, and this on reduction with sulphurous acid loses its chlorine atoms, or, by the action of ethyl chloride, is converted into an open-chain product represented by the ethoxy-derivative of III. Some of the compounds described in this communication possess germicidal properties.

Several papers by Staudinger and his co-workers [37] record advances in the preparation and study of ketens, but their attempts

[35] F. D. Chattaway and O. G. Backeberg, *T.*, 1923, **123**, 2999.

[36] G. T. Morgan and H. G. Reeves, *ibid.*, p. 444.

[37] C. deW. Hurd and C. Kocour, *J. Amer. Chem. Soc.*, 1923, **45**, 2167; *A.*, i, 1060.

to prepare diketens have up to the present met with little success. It is of interest that the pyrogenic decomposition of methyl ethyl ketone leads to the formation of keten and ethane instead of the expected methyl keten and methane.

The problem of separating the constituents of wood spirit which are usually designated as ketones has yielded interesting results.[38] Many of the constituents give crystalline bisulphite compounds, and among other products there have been isolated αα-dimethylpropaldehyde, $CMe_3 \cdot CHO$, *iso*valeraldehyde, and Δγ-hexen-β-one. For the rest, it may be added that one of the first of the vitamins to be isolated, namely vitamin-*A*, from cod-liver oil, is shown to be composed of carbon, hydrogen, and oxygen, and to possess aldehydic properties.[39]

Acids and their Derivatives.

Researches concerned with acids and their derivatives constitute a widely varied literature with which it is difficult to cope in a limited review. Apart from many examples of new preparative processes of the simpler members to which reference must occasionally be made, the group of the acids provides a rich harvest for numerous workers engaged on the investigation of general phenomena such as the mechanism of reaction and tautomeric change. It seems more advantageous to summarise the literature dealing with such fundamental principles rather than to register a series of isolated facts.

The bromination of aliphatic acids pursues two distinct routes, (1) through the enolic form of the acid, (2) through the initial formation of anhydride, and the latter is the more rapid of the two.[40] Theories of halogenation which are based only on the first of these observations are considered incomplete, inasmuch as it is shown that bromination of acetic acid in presence of red phosphorus does not proceed independently of the bromine concentration, as would be the case if the first factor only were operative. Both factors come into play under the conditions described. At first, the reaction proceeds entirely through the anhydride until the concentration of the latter and of bromine diminishes, and with increase of the hydrogen bromide the reaction through the enolic form of the acid is accelerated and finally pursues this course to the end.

Whilst the simpler view of the reaction indicated by Lapworth is followed when acetic acid is brominated in the presence only of hydrogen chloride, the use of phosphorus establishes other conditions

[38] H. Pringsheim and J. Leibowitz, *Ber.*, 1923, **56**, [*B*], 2034; *A.*, i, 1052.
[39] K. Takahashi and K. Kawakami, *J. Chem. Soc. Japan*, 1923, **44**, 580; *A.*, i, 968.
[40] B. D. Shaw, *T.*, 1923, **123**, 2233.

leading to a cycle of changes which may be formulated as below, although the principle of enolisation may apply to the anhydride, once it is formed :

$$CH_3{\cdot}COBr + CH_3{\cdot}CO_2H \rightleftharpoons (CH_3{\cdot}CO)_2O + HBr.$$
$$(CH_3{\cdot}CO)_2O + Br_2 = CH_3{\cdot}COBr + CH_2Br{\cdot}CO_2H.$$

The former of these reactions, although reversible, proceeds to completion because the acetic anhydride is removed by the latter reaction, which is rapid [41] and on exhaustion is followed by the change

$$CH_3{\cdot}CO_2H \rightleftharpoons CH_2{:}C(OH)_2 \longrightarrow CH_2Br{\cdot}CBr(OH)_2$$
$$\longrightarrow CH_2Br{\cdot}CO_2H + HBr.$$

The best conditions for the preparation of bromoacetic acid are found to be those under which a trace of acetic anhydride is used as carrier in the absence of phosphorus, when the yield of pure acid exceeds 95 per cent. of the theoretical, and analogous conditions are applicable also to other cases.

Such considerations also illuminate the mechanism of the reaction involved in the conversion of trichloroethylene into chloroacetic acid [42] by the agency of 90—93 per cent. sulphuric acid, and this new reaction may be represented :

$$CHCl{:}CCl_2 \longrightarrow CH_2Cl{\cdot}CCl_2{\cdot}SO_4H \longrightarrow CH_2Cl{\cdot}CCl_2{\cdot}OH \longrightarrow$$
$$CH_2Cl{\cdot}COCl \longrightarrow CH_2Cl{\cdot}CO_2H.$$

In the case of pyruvic acid, the different phases of the bromination are well defined, and in a suggestive paper [43] the isolation of crystalline bromopyruvic acid, m. p. 59°, is communicated for the first time. With molecular quantities of acid and halogen, activation begins at 50°, but the reaction may be conducted in a freezing mixture by admitting initially a trace of hydrogen bromide or sulphuric acid. The mixture soon solidifies to a mass of bright red crystals; these melt and again solidify to colourless crystals which fume. On warming, these again melt with evolution of hydrogen bromide, and finally solidify, on cooling, to the colourless bromo-acid. The bromination of compounds containing the carbonyl group thus appears to pass through at least four stages to its completion, and may be represented by the scheme

$$\begin{matrix} -CH_2 \\ | \\ -CO \end{matrix} \longrightarrow \begin{matrix} -CH \\ \| \\ -C(OH) \end{matrix} \longrightarrow \begin{matrix} -CHBr \\ | \\ -C(OH)Br \end{matrix} \longrightarrow \begin{matrix} -CHBr \\ | \\ -CO \end{matrix} + HBr,$$

[41] Hentschel, *Ber.*, 1884, **17**, 1286; A. Lapworth, *T.*, 1904, **85**, 41.

[42] L. J. Simon and G. Chavanne, *Compt. rend.*, 1923, **176**, 309; *A.*, i, 177; *Bull. Soc. chim. Belg.*, 1923, **32**, 285; *A.*, i, 894.

[43] C. F. Ward, *T.*, 1923, **123**, 2207.

and there is probably an intermediate stage in which an additive compound is formed from the bromo-acid and hydrogen bromide.

Allocation of configurational formulæ to the geometric isomerides of crotonic acid and its homologues presents difficulties which cannot easily be surmounted. K. von Auwers and his collaborators [44] have endeavoured to elucidate the problem by chemical means, utilising reactions which do not obscure the various stages of synthesis and do not involve any drastic methods of introducing the double linking. The synthesis of γγγ-trichlorocrotonic acid is effected by condensing chloral with malonic acid, and, passing through the stage of the trichloro-β-hydroxybutyric acid, this is ultimately dehydrated. The trichlorocrotonic acid undergoes smooth conversion into fumaric acid at 0° with sulphuric acid, and no trace of maleic acid could be detected, whilst the latter acid under similar conditions is quite stable. Moreover, reduction of the trichloro-acid to solid crotonic acid occurs readily in the cold. It is therefore concluded that solid crotonic acid is the *trans*-form and *iso*crotonic acid is the *cis*-modification. Evidence based on measurements of conductivity [45] pronounces in favour of the relationship of erucic acid to crotonic acid, and of brassidic acid to *iso*crotonic. Combining these results with those given above, erucic acid should be the *trans*- and brassidic acid the *cis*-modification. This conclusion is contrary to that drawn from *X*-ray measurements of the latter two acids,[46] since the spacing of brassidic acid is longer than that of erucic acid to the extent of about 30 per cent. Consequently, the former should be the *trans*-, and the latter the *cis*-modification. The *X*-ray method furnishes a new instrument for the solution of such problems, and it is abundantly evident that many structural difficulties may be resolved by this means. Measurements of maleic and fumaric acids might well be undertaken in order to compare the lengths of spacings and the results applied in the direction indicated above. The interpretation of these experimental results affords evidence from a welcome quarter that the speculation as to the tetrahedral angle of the carbon atom harmonises well with the observed physical measurements and that the formulæ of organic chemistry are not imaginary creations having a limited range of truth.

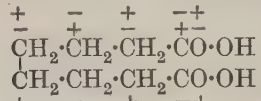
Speculation as to the reason for the predominance in nature of fatty acids of the even series finds a partial explanation in the

[44] *Annalen*, 1923, **432**, 46; *A.*, i, 746; *Ber.*, 1923, **56**, [*B*], 715, 733; *A.*, i, 294, 295.

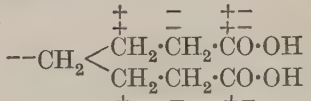
[45] D. Holde and F. Zadek, *ibid.*, p. 2052; *A.*, i, 1058.

[46] A. Müller and G. Shearer, *T.*, 1923, **123**, 3156; compare A. Müller, *ibid.*, p. 2043.

persistent tendency of the dibasic acids of the even series to be produced by oxidation. Compounds which might reasonably be expected to yield the odd series fail to do so. For example, mono- and di-bromoazelaic acids, on treatment with aqueous alkali to eliminate bromine, are oxidised by permanganate to adipic and suberic acids, respectively, instead of to pimelic acid.[47] The explanation is sought in the existence of crossed polarities in the even members, since compounds exhibiting this relationship are considered to be more stable than those in which the positive and negative charges continue to heap up to the end of the chain as is the case with the odd series of acids :



Suberic acid (even).



Pimelic acid (odd).

It is contended that the form of the electronic theory expounded by Lowry fails to lend itself readily to the interpretation of the existence of stereoisomerides of compounds containing conjugated double linkings, of which $\alpha\alpha'$-dibromomuconic ester is an example. Three crystalline, stable forms have been isolated,[48] and these appear to be genuine geometric isomerides, and only at high temperatures is any interconversion observed. The mobility of the linkings suggested by a formula such as Lowry would ascribe to this substance is held not to be consonant with these observations, and it would seem that the double linking maintains its location as a persistent reality scarcely expressed by the type of union represented as a single unit of co-valency modified in the way suggested by Lowry's theory.

Tautomerism or reversible isomeric change of the kind represented by ethyl acetoacetate and definable as the movement of a mobile hydrogen atom may be regarded as the "aliphatic" representation (I). Benzene exhibits another kind, the "aromatic" representation (II), which requires no such transference of hydrogen. Differing from the keto-enolic type, there is a third kind of manifestation (III), in which the occurrence of a semi-aromatic or normal form is postulated

(I.) $CH{-}C{=}O \rightleftharpoons C{=}C{-}OH.$

(II.) $CH{-}CH{=}CH \rightleftharpoons CH{=}CH{-}CH.$

(III.) $R{\cdot}CH{-}C{\equiv}C \rightleftharpoons R{\cdot}C{=}C{-}CH.$

[47] W. A. P. Challenor and J. F. Thorpe, *T.*, 1923, **123**, 2480.
[48] E. H. Farmer, *ibid.*, p. 2531.

It is suggested by J. F. Thorpe[49] that intermediate phases of (I) and (III) should be capable of manifestation :

$$\text{(I}a\text{.)}\quad \mathrm{CH{-}C{=}O} \rightleftharpoons \mathrm{\overset{(H)}{C{-}C{-}O}} \rightleftharpoons \mathrm{C{=}C{-}OH.}$$

$$\text{(III}a\text{.)}\quad \mathrm{R{\cdot}CH{-}C{\equiv}C} \rightleftharpoons \mathrm{R{\cdot}\overset{(H)}{C{-}C{-}C}} \rightleftharpoons \mathrm{R{\cdot}C{\equiv}C{-}CH.}$$

The former of these expressions has not yet been realised experimentally, but the latter is represented by the series of the glutaconic acids in which the "normal" type of isomeride is the intermediate phase. Feist's contention that the isomerism of the substituted glutaconic acids is of the usual geometric kind is resisted, and the evidence in the cases of αβ-dimethylglutaconic acid and β-phenyl-α-methylglutaconic acid is reviewed by Thorpe and Wood.[50] The fact that ozone yields degradation products pointing to two forms only of each of these acids is considered insufficient proof, since the analogous case of the constitution of benzene cannot be decided by such means. It is claimed that Feist's products are those which are anticipated if the esters of the isomeric β-phenyl-α-methylglutaconic acid reacts in the "normal" form. The view that Feist's two acids, m. p. 155° and 151°, are the *trans*- and *cis*-forms and that the two other acids, m. p. 120° and 108°, obtained by Thorpe and his colleagues are impure specimens of these forms is opposed to the fact that they are obtained by the hydration of a pure anhydride which has been recrystallised repeatedly. Thorpe and Wood regard Feist's acids as the *trans*-labile and *cis*-forms, and their own two other acids as the normal and *cis*-labile forms

$\mathrm{CO_2H{\cdot}C{=}CMe}$	$\mathrm{CHMe{\cdot}CO_2H}$	$\mathrm{{\cdot}C{=}CMe{\cdot}CO_2H}$	$\mathrm{CMe{\cdot}CO_2H}$
CPh	CPh	CHPh	CPh
$\mathrm{CH_2{\cdot}CO_2H}$	$\mathrm{CH{\cdot}CO_2H}$	$\mathrm{{\cdot}CH{\cdot}CO_2H}$	$\mathrm{CH_2{\cdot}CO_2H}$
trans-labile, m. p. 155°. (I.)	*cis*-, m. p. 151°. (II.) (Feist)	normal, m. p. 120°. (III.)	*cis*-labile, m. p. 108° (IV.)

The anhydride obtained from (II) differs from that of (III) and (IV), although their melting points are similar, but they react differently on hydration, since Thorpe and Wood's anhydride passes into (III) and (IV), and is, moreover, partly converted into Feist's anhydride on distillation, and thereafter into (II). It seems to the present writer that a fumaroid form of (II) should also exist, namely, $\mathrm{Ph{\cdot}C{=}CHMe{\cdot}CO_2H}$, and, moreover, that the application of the $\mathrm{CO_2H{\cdot}CH}$

[49] *T.*, 1923, **123**, 1361.

[50] J. F. Thorpe and A. S. Wood, *ibid.*, p. 62.

method of *X*-ray measurement to these acids would have special interest.

With the object of investigating the influence of various groups in effecting alteration of the tetrahedral angle between two substituents on the same carbon atom, the behaviour of several β-substituted dibromoglutaric esters of the type $\begin{matrix}a\\b\end{matrix}\!>\!C\!<\!\begin{matrix}CHBr\cdot CO_2Et\\CHBr\cdot CO_2Et\end{matrix}$ has been studied.[51] Where *a* and *b* are methyl and ethyl, the ester loses ethyl bromide on distillation and passes into the lactone $\begin{matrix}Me\\Et\end{matrix}\!>\!C\!<\!\begin{matrix}CH(CO_2Et)\cdot O\\CHBr\text{———}CO\end{matrix}$. The free dibasic acid exists in *cis*- and *trans*-forms, and changes by the agency of sodium carbonate into the analogous lactonic acid. In contact with methyl alcoholic potash, the dibromo-ester resembles the dimethyl analogue in yielding a *cyclo*propane derivative,

$$\begin{matrix}Me\\Et\end{matrix}\!>\!C\!<\!\begin{matrix}C(OMe)\cdot CO_2H\\CH\cdot CO_2H\end{matrix},$$

which exists in *cis*- and *trans*-forms. The methoxyl group in this compound is eliminated in the usual way with hydriodic acid, but the expected hydroxy-ring acid suffers fission and passes into the open-chain ββ-methylethyl-α-ketoglutaric acid, $\begin{matrix}Me\\Et\end{matrix}\!>\!C\!<\!\begin{matrix}CO\cdot CO_2H\\CH_2\cdot CO_2H\end{matrix}$, which yields *as*.-methylethylsuccinic acid on distillation. When *a* and *b* are both methyl groups, a quantitative transformation occurs into ββ-dimethylketoglutaric acid. The first evidence of stability of the *cyclo*propane ring occurs when *a* and *b* are both ethyl groups, and in this case the keto-acid and the hydroxy-ring acid are tautomeric, and this is borne out in the dipropyl series. The larger alkyl groups in the latter produce a widening of the angle between the two α-residues, and confer greater stability on the *cyclo*propane ring. Similar principles are operative when sodium hydroxide reacts with tribromo-ββ-dipropylglutaric acid,[52]

$$Pr_2C\!<\!\begin{matrix}CBr_2\cdot CO_2H\\CHBr\cdot CO_2H\end{matrix} \rightarrow Pr_2C\!<\!\begin{matrix}CO\cdot CO_2H\\CHBr\cdot CO_2H\end{matrix} \text{ (I.)} \rightarrow$$

$$\text{(II.) } Pr_2C\!<\!\begin{matrix}CO_2H\\CHBr\cdot CO_2H\end{matrix} \rightarrow Pr_2C\!<\!\begin{matrix}CO\\>O\\CH\cdot CO_2H\end{matrix} \text{ (III.)}$$

when the keto-acid (I) leads to the substituted succinic acid (II) by loss of carbon monoxide and finally to the β-lactone (III) by elimination of hydrogen bromide. This β-lactone is a stable

[51] B. Singh and J. F. Thorpe, *T.*, 1923, **123**, 113; F. R. Goss, C. K. Ingold, and J. F. Thorpe, *ibid.*, p. 327; L. Bains and J. F. Thorpe, *ibid.*, p. 1206.

[52] L. Bains and J. F. Thorpe, *ibid.*, p. 2742.

crystalline compound; the lactone ring is opened by boiling with dilute alkali, and closes again on neutralisation at 0°, so that the lactone is regenerated, as is not usually the case with β-lactones. The effect of the two propyl residues is to cause the carboxyl and β-hydroxyl groups to become approximately the same distance apart as in a γ-hydroxy-acid and hence the β-lactone assumes a stability comparable with that of γ-lactones.

The condensation of ββ- and αβ-dimethylacrylic esters with oxalic ester occurs in the γ-position by the agency of potassium ethoxide.[53] Thus the αβ-substituted ester reacts as follows:

$$\begin{matrix}CO_2Et\\CO_2Et\end{matrix} + CH_3{\cdot}CH{:}CMe{\cdot}CO_2Et \longrightarrow \begin{matrix}C(OH){:}CH{\cdot}CH{:}CMe{\cdot}CO_2Et\\CO_2Et\end{matrix}$$

This corresponds to a Claisen condensation in which the usual requirement of hydrogen atoms in the α-carbon atom is dispensed with owing to development of the necessary hydrogen activity at the γ-carbon atom. The doubly unsaturated product of the condensation changes into an α-pyrone in contact with concentrated hydrochloric acid, whilst the analogous pyrone from the ββ-dimethylacrylic ester is produced direct from the condensation with oxalic ester. In the same paper, an improved method of preparing the cyanohydrin of methyl ethyl ketone is described. The same authors contribute an interesting example of the reduction of an unsaturated ester analogous in its mechanism to the pinacolin formation.[54] Ethyl ethylidenemalonate undergoes reduction with palladium and hydrogen to give the expected ethyl ethylmalonate, but with sodium amalgam the change is represented by the following:

$$2CH_3{\cdot}CH{:}C(CO_2Et)_2 \longrightarrow \begin{matrix}CH_3{\cdot}CH{\cdot}CH(CO_2Et)_2\\CH_3{\cdot}CH{\cdot}CH(CO_2Et)_2\end{matrix}$$

A discussion of the mechanism involved in the reaction between aldehydes and sodium cyanoacetate is communicated which favours the adoption of formulæ displaying αβ-unsaturation in all such cases.[55]

$$R{\cdot}CHO + CH_2(CN){\cdot}CO_2X \longrightarrow R{\cdot}CH{:}C(CN){\cdot}CO_2X.$$

The addition to such products of reagents like potassium cyanide, sodium bisulphite, or hydroxylamine is regarded as diagnostic of the αβ-type of unsaturation and these tests are utilised in support of the validity of this view. On the other hand, analogous cases

[53] Lucy Higginbotham and A. Lapworth, *T.*, 1923, **123**, 1325.

[54] *Ibid.*, p. 1618.

[55] A. Lapworth and J. A. McRae, *T.*, 1922, **121**, 1699, 2741; S. F. Birch, G. A. R. Kon, and W. S. G. P. Norris, *T.*, 1923, **123**, 1361.

are known where similar products display tautomerism and exist equally in their βγ-unsaturated forms, a condition which is probably more especially operative where a cyclic ketone participates in the reaction with the cyanoacetate.

Halogen Compounds.

A reinvestigation of the conditions operative in the chlorination of methane has led to an appreciation of the value of adequate means of control, and the causes of the departure from the stepwise reaction are discussed in detail.[56] A yield of methyl bromide amounting to 96 per cent. is made available by the use of 1·25 mols. of methyl alcohol, 1 mol. of potassium bromide, and 3 mols. of sulphuric acid diluted with a third of its weight of water. This appears to be the most economical procedure for preparing the reagent. An excellent yield of pure bromopicrin is obtainable by exposure of aqueous picric acid and bromine in presence of sodium carbonate to direct sunlight for a few days. The reaction proceeds also in the absence of light, but takes longer, and the sodium salt of picric acid seems to be the active agent. It is now shown that the yellow, explosive compound produced from bromopicrin with 50 per cent. potassium hydroxide is not a potassium salt of bromonitromethane, but is *s*.-dipotassium tetranitroethane.[57] The addition of an ester of hypobromous acid to an olefinic [58] linking occurs readily in presence of acids, particularly formic acid, with the use of bromotrinitromethane, thus :

$$\cdot CH{:}CH\cdot + HO\cdot CHO + CBr(NO_2)_3 \longrightarrow \cdot CH(O\cdot CHO)\cdot CHBr\cdot + CH(NO_2)_3.$$

In the section on hydrocarbons, examples will be found of the mode of attachment of halogen and halogen acids to olefinic compounds, and these are more advantageously placed under that head, since their chief interest lies in an explanation of the behaviour of double linkings. Numerous communications have been made during the year on the mode of preparation and properties of such additive compounds, and references to a few of these are now given. . The action of pure bromine on propylene gives rise to a yield of 90 per cent. of propylene bromide and 4 per cent. of αβγ-tribromopropane. The presence of metallic iron as catalyst leads to 40 per cent. of the latter product and 17 per cent. of ααβ-tribromopropane, whilst with ferric bromide or aluminium as

[56] A. Schleede and C. Luckow, *Ber.*, 1922, **55**, [*B*], 3710; *A.*, i, 83.
[57] L. Hunter, *T.*, 1923, **123**, 543.
[58] E. Schmidt, R. Schumacher, and R. Asmus, *Ber.*, 1923, **56**, [*B*], 1239; *A.*, i, 645.

catalyst the latter two bromopropanes are produced in the proportion 8 : 33. Rules for conducting such brominations [59] are given and represent an extension of the substitution rules of Markovnikov, Städel, and V. Meyer.

In a paper by A. E. Favorski [60] various examples of intramolecular rearrangement of hydrocarbons and their halogen derivatives are given, and from these it is concluded that a condition of strain may develop between the carbon linkings, leading to dissociation. Tertiary carbon atoms multiply joined to other atoms often undergo rearrangement resulting in the transposition of their elements, and one example from many may be quoted :

$$CH_2Me{\cdot}CMeBr{\cdot}CH_2Me \longleftarrow CH_2Me{\cdot}CMe_2{\cdot}CH_2Br \longrightarrow CH_2Me{\cdot}CH_2{\cdot}CMe_2Br.$$

The spontaneous decomposition of unsaturated aliphatic iodochlorides has been studied,[61] and in the case of β-chloroethylene iodochloride the products are iodine monochloride, trichloroiodoethane, ααββ-tetrachloroethane, and a dichloroiodoethane, and of these the first two are the principal products. The changes consist of several rearrangements involving the elimination and subsequent addition of the halogen atoms.

Under the hydrocarbon group there are also recorded the results of an investigation on the mechanism of the Würtz-Fittig reaction. A contribution to the study of the behaviour of sodium with organic substances in liquid ammonia solution [62] may here be mentioned. Treatment of an organo-magnesium compound, such as magnesium ethyl iodide, in ethereal solution with dry ammonia [63] gives rise to a substance analogous to sodamide, but more easily obtainable and having constant properties :

$$MgEtI + NH_3 \longrightarrow NH_2{\cdot}MgI + C_2H_6.$$

A study of the properties of the magnesylamine has been made and this would appear to be a useful reagent for the preparation of organic amides.

New methods for the preparation of αδ-dibromobutane [64] should prove useful in synthetic work, and these are described by two independent investigators.

[59] B. K. Mereshkowsky, *Annalen*, 1923, **431**, 113, 231; *A.*, i, 527, 643.
[60] *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 43; *A.*, i, 430.
[61] L. B. Howell, *J. Amer. Chem. Soc.*, 1923, **45**, 182; *A.*, i, 174.
[62] C. A. Kraus and G. F. White, *ibid.*, pp. 768, 779; *A.*, i, 456, 457.
[63] G. Oddo and E. Calderaro, *Gazzetta*, 1923, **53**, i, 64; *A.*, i, 448.
[64] C. S. Marvel and A. L. Tanenbaum, *J. Amer. Chem. Soc.*, 1922, **44**, 2645; *A.*, i, 2; J. von Braun and G. Lemke, *Ber.*, 1922, **55**, [*B*], 3526; *A.*, i, 2.

Carbohydrates.

General.—New sources and methods of preparation of sugars and their derivatives are made available,[65] among which may be mentioned arabinose, rhamnose, xylose, galactose, fructose, maltose, trehalose, raffinose, and gluconic acid. The sodium derivative of glucose which has so frequently figured in the literature is now shown to be merely an additive compound of glucose and sodium ethoxide.[66] Improvement in the technique of the oxidation of sugars with nitric acid continues to lead to the isolation of new sugar derivatives. At atmospheric temperature the reaction functions in several unexpected directions. It seems clear that the secondary alcohol group may pass with ease into a keto-group, and this is more especially the case with the fifth group of a hexose,[67] thus emphasising the special character of this group which has previously been observed in other connexions.

Monosaccharides and Glucosides.—A reinvestigation of the acetone derivatives of sugars appears to reveal several anomalies requiring explanation, and in the discussion which has arisen as to the structure of these compounds the observation that trimethylene glycol [68] condenses with acetone invites caution in drawing conclusions. A constitution of glucose diacetone is given which is in conflict with that previously assigned to this compound on the basis of its methylation.[69] Much confusion would be avoided if it were always possible to decide which of the various oxide linkings is present in the sugar which combines with acetone.

This fundamental problem of the structure of sugars is receiving the attention it merits, and it appears to be established that aldoses can exist either as 1 : 4- or 1 : 5-oxides (butylene or amylene oxides), the equivalent form for ketoses being 2 : 5- or 2 : 6-oxides. Which of these two forms will possess the greater stability may depend on such factors as torsional strain and variation of tetrahedral angle, considerations such as have been applied to the ββ-disubstituted glutaric acids by Thorpe, Ingold, and others. It is by no means to be accepted that the different configurations of the hydroxyl groups displayed by the various hexoses will always

[65] T. Swann Harding, *Sugar*, 1922, 406; 1923, 82, 124, 175, 240, 308, 350, 406, 476; *A.*, i, 898, 1062, 1064; A. Blanchetière, *Bull. Soc. chim.*, 1923, [iv], **33**, 345; *A.*, i, 539; L. Bert, *ibid.*, p. 733; *A.*, i, 754; D. H. Brauns, *J. Amer. Chem. Soc.*, 1923, **45**, 833; *A.*, i, 441.

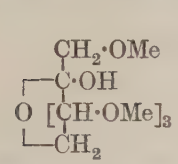
[66] G. Zemplén and A. Kunz, *Ber.*, 1923, **56**, [*B*], 1705; *A.*, i, 897.

[67] H. Kiliani, *Ber.*, 1922, **55**, [*B*], 2817; *A.*, 1922, i, 1111.

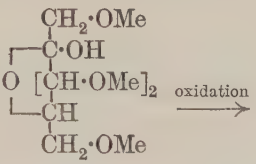
[68] J. Böeseken and P. H. Hermans, *ibid.*, p. 3758; *A.*, i, 86; compare *Rec. trav. chim.*, 1922, **41**, 722; *A.*, i, 177.

[69] K. Freudenberg and A. Doser, *Ber.*, 1923, **56**, [*B*], 1243; *A.*, i, 652; P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, 1922, **54**, 805; *A.*, i, 92.

lend themselves to the development of the same degree of stability of the oxide ring, and hence it is to be expected that some sugars will be more stable as the 1 : 5-oxide than as the 1 : 4-oxide form. The adoption of either the butylene- or amylene-oxide structure to represent the normal and the so-called γ-sugars may well result in the possible allocation of a 1 : 4-oxide formula to the latter in the case of some simple sugars. Meanwhile, it is demonstrated that the dextrorotatory tetramethyl γ-fructose [70] isolated from methylated sucrose has the 2 : 6-oxide structure (I) (see under disaccharide section).



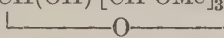
(I.)
Tetramethyl γ-fructose (dextrorotatory).



(II.)
Tetramethyl fructose (lævorotatory).

(III.)
Dimethoxyhydroxyglutaric acid.

A second example of this type of linking is found in the case of xylose, since trimethyl xylose gives an inactive specimen of trimethoxyglutaric acid on oxidation.[71] This methylated sugar has therefore the constitution $CH(OH)\cdot[CH\cdot OMe]_3\cdot CH_2$, although its



properties correspond with those of a normal sugar and not with a γ-form. Conversely, to the normal or lævorotatory form of tetramethyl fructose is given the usual 2 : 5-oxide formula (II), inasmuch as it is degraded by oxidation [72] with nitric acid to the dimethoxyhydroxyglutaric acid (III), which has been isolated as the ethyl ester. The normal tetramethyl galactose conforms, however, to the 1 : 5-oxide type, as is demonstrated in an investigation based on the Hudson rule as applied to the rotation of its tetramethylgalactonolactone.[73] Evidence of the structure of a less stable variety of this sugar is, however, awaiting publication by the present writer, and this appears to have the constitution of a 1 : 4-oxide.

Confusion as to the meaning of the term γ-sugar may well arise, since only substitution derivatives of this type have hitherto been isolated. Strictly speaking, the term might be restricted to that structural form of a sugar or its derivative which corresponds in properties with the earliest example published by E. Fischer and

[70] W. N. Haworth and W. H. Linnell, *T.*, 1923, **123**, 294.
[71] E. L. Hirst and C. B. Purves, *T.*, 1923, **123**, 1352.
[72] J. C. Irvine and J. Patterson, *T.*, 1922, **121**, 2696.
[73] J. Pryde, *T.*, 1923, **123**, 1808.

described by him as γ-methylglucoside. The free γ-glucose should presumably possess the same internal structure as its glucoside, were it capable of isolation, but it is suggested [74] that such a sugar may be incapable of real existence, and that the abnormal activity associated with the properties of a γ-sugar may find its only interpretation in the aldehydic or ketonic phase of a monose.

The synthesis of substituted *n*-hexanes containing hydroxyl as well as a ketone or aldehyde residue so constituted as to be equivalent to a de-oxygenated hexose continues to be of service in presenting analogies with sugars. The two following compounds have been prepared,[75]

$$CH_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CHO$$
$$CH_2(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO{\cdot}CH_3,$$

and the former of these gives rise to two semi-acetals with methyl alcohol containing in the one case a 1 : 2-oxide and in the other a 1 : 4-oxide structure, and these exhibit different rates of hydrolysis in accordance with the experience with sugars, and, moreover, 2 mols. of the aldehyde condense to give an anhydride analogous to a biose. The second compound formulated above furnishes a dicyclic anhydride which, although containing an ethylene oxide ring (1 : 2-oxide), is unusually resistant to fission, whilst it has previously been shown that the amylene-oxide or 1 : 5-ring is, in similar compounds, remarkably sensitive to hydrolytic agents.

The constitution of *l*-glucosan is again a subject of controversy, and the formula originally assigned by Pictet is supported by evidence adduced from methylation.[76] Trimethyl glucosan is found to give rise to a reducing sugar on boiling with water, and this appears to be 3 : 5 : 6-trimethyl glucose, since it forms a crystalline osazone. The authors have not, however, taken the necessary precaution of estimating the methoxyl content of their osazone, and have confined their analyses to an estimation of nitrogen. The expulsion of a methoxyl group during osazone formation is not an unknown experience, and such an occurrence would invalidate the authors' reasoning. Earlier workers,[77] on the contrary, diagnosed the sugar as 2 : 3 : 5-trimethyl glucose and modified the Pictet formula for *l*-glucosan to harmonise with this result. Other new facts relating to methylated hexoses include the isolation of a crystalline tetramethyl α-galactose and of a crystalline 2 : 3 : 6-tri-

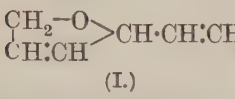
[74] J. C. Irvine, *T.*, 1923, **123**, 898.

[75] B. Helferich and A. Russe, *Ber.*, 1923, **56**, [*B*], 759; *A.*, i, 301; B. Helferich and R. Weidenhagen, *ibid.*, 1922, **55**, [*B*], 3348; *A.*, 1922, i, 1115; M. Bergmann and A. Miekeley, *Annalen*, 1923, **432**, 319; *A.*, i, 1053.

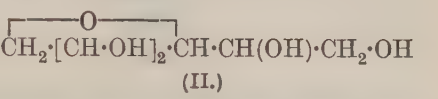
[76] M. Cramer and E. H. Cox, *Helv. Chim. Acta*, 1922, **5**, 884; *A.*, i, 94.

[77] J. C. Irvine and J. W. H. Oldham, *T.*, 1921, **119**, 1744.

methyl β-methylglucoside.[78] Exchange of the glycerol residue for that of a hexose is reported in the case of olive oil, which, on heating with α-methylglucoside in presence of sodium ethoxide, forms a mono-oleate of the glucoside, whilst in the case of mannitol a dioleate of this hexitol is isolated.[79] With both examples, the reaction is accompanied by internal dehydration of the carbohydrate chain. Anhydromethylglucoside mono-oleate and mannitan dioleate are homogeneous compounds, and following methylation and hydrolysis give rise to methylated anhydro-sugar derivatives. A structural formula proposed [80] for mannitan (II),



(I.)



(II.)

is confirmed by a series of reactions involving the formation of the furan derivative (I) by decomposition of mannitol hexaformate, and the reduction of the compound (I) to 2-ethyltetrahydrofuran. The claim is made of the discovery of a new method of characterising the acids derived from sugars, depending on the observation [81] that dibasic acids derived from hexoses and monobasic acids from pentoses give colour reactions with ferric chloride, whilst the monobasic acids from hexoses do not do so. A synthesis of pentamethyl arbutin [82] has been achieved by the condensation of tetramethyl glucose in benzene with quinol monomethyl ether in presence of hydrogen chloride and anhydrous sodium sulphate. Arbutin is thus shown to contain the normal glucose residue.

Disaccharides and Trisaccharides.—A new constitutional formula has been applied to sucrose and experimental evidence brought to its support in two papers [83] which outline a study of the structure of the fructose unit isolated by hydrolysis of methylated sucrose. This fructose derivative has already been the subject of earlier work, and the presence of an ethylene-oxide linking was favoured, although alternative formulæ were kept in view. It is now demonstrated that the oxidation of tetramethyl γ-fructose, a cleavage product of octamethyl sucrose, leads to two simple degradation

[78] H. H. Schlubach and K. Moog, *Ber.*, 1923, **56**, [*B*], 1957; *A.*, i, 1063.

[79] H. S. Gilchrist, *Rep. Brit. Assoc.*, 1922, 357; *A.*, i, 297.

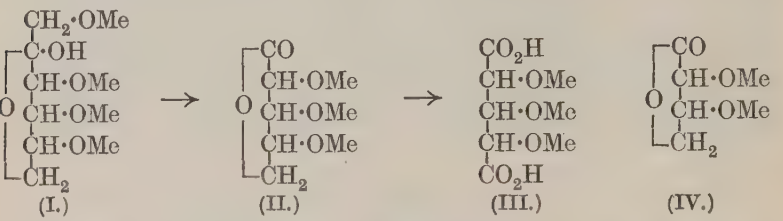
[80] P. van Romburg and J. H. N. van der Burg, *Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 335; A., i, 85.

[81] L. J. Simon and A. J. A. Guillaumin, *Compt. rend.*, 1922, **175**, 1208; *A.*, i, 239.

[82] A. K. Macbeth and J. Mackay, *T.*, 1923, **123**, 717.

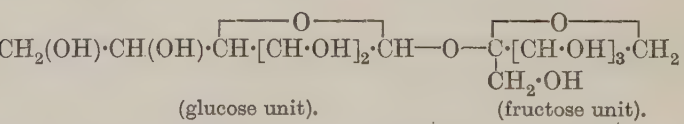
[83] W. N. Haworth and W. H. Linnell, *T.*, 1923, **123**, 294; W. N. Haworth and J. G. Mitchell, *ibid.*, p. 301; compare M. Bergmann, *Ber.*, 1923, **56**, [*B*], 1227; *A.*, i, 654.

products, both of which afford guidance as to the constitution. Oxidation with nitric acid furnishes a trimethoxyvalerolactone (II) which, on further oxidation, gives rise to a trimethoxyglutaric acid (III), whilst direct oxidation of the sugar with permanganate produces a dimethoxybutyrolactone (IV) :



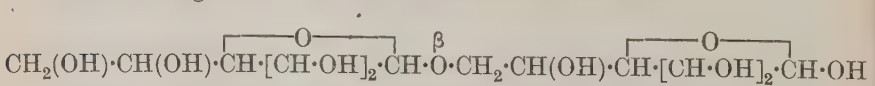
(I.) (II.) (III.) (IV.)

On the basis of these results, tetramethyl γ-fructose receives the formula (I), since it is apparent that the dibasic acid (III) could only be produced if the lower terminal carbon atom in (I) yielded a carboxyl group by reason of the opening of the six-membered ring. Applying these facts to sucrose, the following constitution is given to this disaccharide :



(glucose unit). (fructose unit).

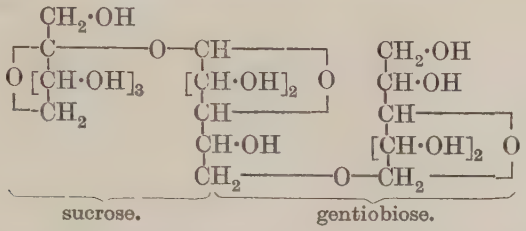
By observation of the mutarotation of the glucose which is liberated by the hydrolysis of amygdalin with emulsin, the biose of amygdalin has been recognised [84] to be a glucosido-β-glucose, the structure of which had already been elucidated by Haworth and Leitch. Gentiobiose has also been the subject of a constitutional study, and the fact emerges that this sugar is identical with that occurring as the biose of amygdalin.[85] Heptamethyl methylgentiobioside undergoes hydrolysis to the easily recognised, crystalline 2 : 3 : 5 : 6-tetramethyl glucose, and to the 2 : 3 : 5-trimethyl glucose, the latter being identified as its crystalline β-glucoside. It therefore follows that gentiobiose has the structure shown below :



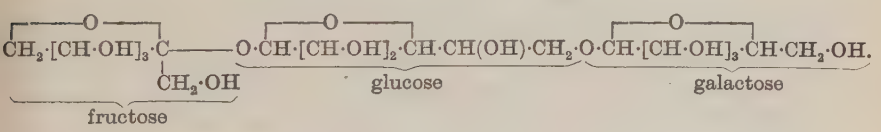
and the linking between the two glucose units is of the β-type. The structure is thus identical with that of maltose which, however, differs stereochemically and is glucosido-α-glucose, whilst both structurally and stereochemically amygdalin biose is the same

[84] R. Kuhn, *Ber.*, 1923, **56**, [*B*], 857; *A.*, i, 589.
[85] W. N. Haworth and B. Wylam, *T.*, 1923, **123**, 3120.

as gentiobiose. Proof of this is also furnished by synthesis of hepta-acetyl amygdalinic acid. Arising from the allocation of this constitution, it is now seen that the trisaccharide, gentianose, has the following formula, since gentianose yields sucrose and gentiobiose respectively with emulsin and invertase.



Methylation of raffinose has led to the elucidation of its structural formula by analogous methods. Hendecamethyl raffinose gives on hydrolytic cleavage three methylated hexoses, which are recognisable as 1 : 3 : 4 : 5-tetramethyl γ-fructose, identical with that obtained from sucrose, 2 : 3 : 5-trimethyl glucose, identical with that derived from maltose, gentiobiose, and amygdalin, and 2 : 3 : 4 : 6-tetramethyl galactose, which had previously been isolated from lactose. The constitution of raffinose is thus indicated, and may be represented by the formula [86]



It follows that raffinose contains a sucrose residue as well as a residue representing melibiose.

Polysaccharides.—The study of the constitution of starch has been advanced by the active inquiry of many workers, and, although finality is still far from achievement, the publications of the year have cleared the ground of numerous pitfalls for the unwary and opened up a path which should lead to substantial progress. Much conflict of opinion might have been avoided even in recent work had it not been that investigators have tended to disregard valuable evidence which is to be gathered from some of the earlier literature on this subject.

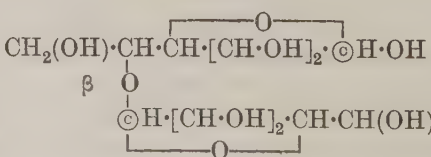
It has long been recognised that the nature of the material comprising the inner portions of the starch granule differs from that of the outer portion. The former of these is known under

[86] W. N. Haworth, E. L. Hirst, and D. A. Ruell, *T.*, 1923, **123**, 3125.

different names, among which are granulose, amylocellulose, amylose; and the name amylopectin has been given to the outer material. The purer starches (for example, from potato, arrow-root) contain almost exclusively these two ingredients, whilst other specimens from rice, wheat, and barley contain also hemicellulose,[87] which, in the case of rice starch, may occur to the extent of 18 per cent. The need for caution in selecting initial material intended to serve as a basis for experimental investigation of the structure of the starch molecule is thus apparent. One is therefore impressed by the searching inquiry into the problem undertaken by Ling and Nanji,[88] who have achieved results of positive and outstanding value. Basing their work on the earlier observations of Baker,[89] who showed that ungerminated barley diastase effects cleavage of starch speedily into crystalline maltose and α-amylodextrin, they have followed biochemical methods for separating the two starch ingredients. With precipitated, desiccated barley diastase at 50°, the amylose constituent is quantitatively converted into maltose, leaving the amylopectin unchanged. Baker's α-amylodextrin is a simpler depolymerised product of amylopectin, from which the phosphoric ester groups have been removed, and Baker's product is now designated αβ-hexa-amylose. Malt diastase, however, effects the cleavage of amylopectin at 70° into a trisaccharide or hexatriose which is at one and the same time α-glucosido*iso*maltose and β-glucosidomaltose, a new product of degraded starch of signal importance. This breaks down with different enzymes to give either *iso*maltose or maltose. It is clear that the degradation of amylopectin may be expressed thus: amylopectin → αβ-hexa-amylose → a trisaccharide (hexatriose) → *iso*maltose or (alternatively) maltose.

The structural formula assigned tentatively to *iso*maltose is represented by I, and that of the triose by II, the ringed carbon atoms indicating the reducing or potential reducing groups:

(I.) *iso*Maltose.

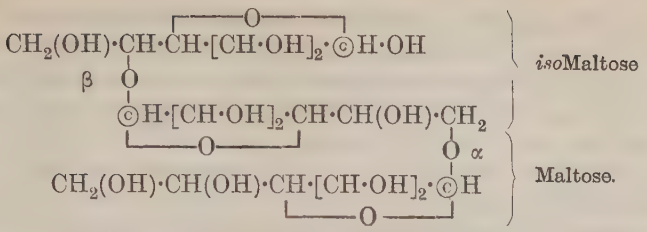


[87] D. H. F. Clayson and S. B. Schryver, *Biochem. J.*, 1923, **17**, 493; *A.*, i, 1066; S. B. Schryver and Ethel M. Thomas, *ibid.*, p. 497; *A.*, i, 1066.

[88] A. R. Ling and D. R. Nanji, *T.*, 1923, **123**, 2666; compare L. Maquenne, *Compt. rend.*, 1923, **176**, 804; *A.*, i, 442.

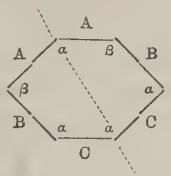
[89] *T.*, 1902, **81**, 1177.

(II.)



The structure allocated to *iso*maltose will doubtless be revised, inasmuch as this formula is already appropriated by cellobiose.[90] Considering the synthetic methods employed in obtaining *iso*-maltose from glucose, it is not inconceivable that one glucose residue in this biose possesses an amylene-oxide structure, and in this case the attachment of the β-linking of the second glucose unit may be through the hydroxyl group associated with the fourth or sixth carbon atom. Certainly *iso*maltose cannot be the β-analogue of maltose, since this formula is already allocated to gentiobiose.[91]

The authors assign a formula to the basal unit of the amylopectin constituent of starch which represents this as αβ-hexa-amylose. The grouping of the six glucose units in this formula is based on the structure given to the hexatriose (II), and may be represented in skeleton as a hexagonal formula in which each side is occupied by a glucose residue as follows :



The lettering at the angles indicates the type of the stereochemical linking, and the letters along the sides show the structure of the units, A and B together representing one *iso*maltose residue, and C and C one maltose residue. Hydrolysis along the dotted line would give rise to two molecules of the triose (II).

As to the structure of polymerised amylose, the second constituent of pure starch, which amounts to about 60 per cent. of the whole, it is made abundantly clear that, since this gives rise to a quantitative yield of maltose on treatment with diastase, the whole of the glucose residues are of the α type. Ling and Nanji again suggest a hexa-amylose structure showing lines of cleavage by depolymerisation into a tetra- and a di-amylose to conform with the known behaviour.

[90] W. N. Haworth and E. L. Hirst, *T.*, 1921, **119**, 193.
[91] W. N. Haworth and B. Wylam, *T.*, 1923, **123**, 3120.

It thus appears possible to reconcile their views on this basis with those of Pringsheim and of Karrer. Pringsheim [92] has long contended that α-hexa-amylose (which is considered to be identical with Ling and Nanji's depolymerised amylose) is a trimeric diamylose, and Karrer [93] strongly maintains that a diamylose is the basal unit of starch and is to be recognised as anhydromaltose. The second or β-series of amyloses has been the subject of controversy. Pringsheim's β-hexa-amylose is similar to Ling and Nanji's αβ-hexa-amylose from amylopectin, and whilst Pringsheim's investigation shows this to be a dimeric triamylose, $[(C_6H_{10}O_5)_3]_2$, Karrer protests that it is a simple triamylose. Differences are thus narrowed down to a slender issue, and the review of the research describing the isolation of a triose from this unit of starch will still further harmonise the outstanding disagreement.

Ling and Nanji express their difficulty in interpreting Irvine and Macdonald's experiments [94] on this basis, and hesitate to attempt any reconciliation with their own experiments, especially in view of the fact that the latter authors used rice starch, and this usually contains an appreciable quantity of hemicellulose which may have confused the issue. In the absence of quantitative figures it is not possible to interpret these results as having reference only to the amylopectin constituent, although there is apparently some relationship between the triamylose formula of Irvine and Macdonald and the triose formula (II) outlined above.

The polyamyloses obtained from starch and glycogen are characterised by the ease with which they undergo depolymerisation to their fundamental substances when acetylated, and also by the resistance they present to complete methylation.[95] These properties are opposed to those displayed by tetraglucosan and tetra*lævo*-glucosan, which can be acetylated under similar conditions without undergoing any depolymerisation, and are methylated with unusual ease. These facts demonstrate that the structure of starch is in no way concerned with the glucosans.

Last year the isolation of cello*iso*biose was reported as a new cleavage product of cellulose, but this is now shown to be a mixture of cellobiose and a new trisaccharide, procellose.[96] The latter is

[92] H. Pringsheim and K. Goldstein, *Ber.*, 1923, **56**, [*B*], 1520; *A.*, i, 899; compare H. Pringsheim and W. Fuchs, *ibid.*, p. 1762; *A.*, i, 965; also "Die Polysaccharide" (H. Pringsheim), 1923, 167.

[93] P. Karrer, *Helv. Chim. Acta*, 1923, **6**, 402; *A.*, i, 655; *Ber.*, 1922, **55**, [*B*], 2854; *A.*, 1922, i, 1119.

[94] See *Annual Reports*, 1922, 81; also J. C. Irvine, *T.*, 1923, **123**, 898.

[95] H. Pringsheim and K. Schmalz, *Ber.*, 1922, **55**, [*B*], 3001; *A.*, 1922, i, 1118.

[96] G. Bertrand and (Mlle) S. Benoist, *Compt. rend.*, 1923, **176**, 1583; **177**, 85; *A.*, i, 756, 757.

a by-product obtained in the usual process of preparing cellobiose octa-acetate, and the determination of its constitution should be helpful in deciding the structure of the unit of cellulose. A constitutional formula for cellulose was discussed in the last Report (p. 82) and a more detailed account of the experimental work on methylated cellulose is now contributed.[97] Mannan, which occurs in vegetable ivory, gives rise on methylation with methyl sulphate to a dimethyl mannan, from which by hydrolysis a lævorotatory dimethyl mannose has been isolated.[98] This sugar conforms to the stable type of mannose despite its unexpected sign of rotation, since it gives the normal crystalline tetramethyl α-methylmannoside on further methylation.

Nitrogen Compounds.

The volume of new researches on nitrogen compounds of the aliphatic series increases from year to year, and the reporter experiences difficulty in writing an adequate epitome of important results. More than a hundred references have been consulted and the space available does not allow of the mention of more than a few of these. Fortunately, a number of the important nitrogen compounds relating to physiological and agricultural chemistry will be reviewed in the separate sections devoted to these branches of the work.

A new laboratory preparation of hydrocyanic acid in large quantities is described,[99] in which potassium ferrocyanide, sulphuric acid, and water in the proportions 10 : 5 : 8 are recommended, and a novel form of apparatus is given. A new synthesis of this acid is mentioned [1] from ethylene and nitrogen under the influence of the silent discharge, and in a theoretical paper,[2] the properties of hydrogen cyanide are considered to be those represented simultaneously by an ammonocarbonous acid, a formaldehyde of the ammonia type, and of a compound related to ammonia as the hypothetical formic anhydride is to water, and this thesis is ably developed. A study of the behaviour of cyanamide in both acid and alkaline solution [3] explains the action of the latter reagent as being due to its hydroxyl-ion, the products being carbamide and the dimeride dicyanodiamide, and the effect of acids is explained on the ionic theory. Other workers regard the polymerisation of

[97] J. C. Irvine and E. L. Hirst, *T.*, 1923, **123**, 518.

[98] J. C. Patterson, *ibid.*, p. 1139.

[99] E. Fritzmann, *J. Russ. Phys. Chem. Soc.*, 1920, **52**, 227; *A.*, 1922, i, 1128.

[1] L. Francesconi and A. Ciurlo, *Gazzetta*, 1923, **53**, i, 327; *A.*, i, 764.

[2] E. C. Franklin, *J. Physical Chem.*, 1923, **27**, 167; *A.*, , 447.

[3] H. C. Hetherington and J. M. Braham, *J. Amer. Chem. Soc.*, 1923, **45**, 824; *A.*, i, 447.

cyanamide to dicyanodiamide as an example of the "urea dearrangement," a change which is shown to occur with carbamide, thiocarbamide, guanidine, and their derivatives.[4]

Hexamethylenetetramine [5] appears on examination to contain no ethylenic bond nor is it to be regarded as a strong base. It combines additively with three molecular proportions of phenol or of the cresols.

An almost quantitative yield of acetamide is available [6] if equal molecular proportions of ammonium acetate and glacial acetic acid are heated for thirty to fifty minutes at a temperature just below the boiling point and then slowly distilled. The temperature of the issuing vapour from the fractionating column is not allowed to exceed 104°, and thus a residue of pure acetamide is obtained. A yield of 54 per cent. of glycine may now be derived [7] from the reaction involving the condensation of formaldehyde with ammonium cyanide and hydrolysis of the resulting nitrile with 40 per cent. baryta, and the characteristics of the two crystalline forms of glycine are described. Hydrolysis of a solution of glycine under new conditions is shown to lead to the formation of ammonium glycollate.[8] Methylglyoxime has not hitherto been isolated in stereoisomeric forms, but the announcement of this result is now made.[9]

The claim that amines, pyridine bases, and alkaloids may be obtained by photosynthetic methods is criticised on the ground that Baly, Heilbron, and Stern subjected their exposed solutions of ammonia and formaldehyde to a heating process with excess of hydrochloric acid as a means of isolating their products. It is shown that this last procedure alone, without exposure of the solutions to light, leads to the formation of the methylamines and their simple condensation products with formaldehyde, a reaction which is already well known.[10] These simple compounds undergo colour reactions and other tests which resemble those previously relied upon in the claims of the earlier workers.

Methylamine condenses with formaldehyde and *n*-butyl alcohol

[4] T. L. Davis and H. W. Underwood, *J. Amer. Chem. Soc.*, 1922, **44**, 2595; *A.*, i, 22; T. L. Davis and K. C. Blanchard, *ibid.*, 1923, **45**, 1816; *A.*, i, 902.

[5] R. Pummerer and J. Hofmann, *Ber.*, 1923, **56**, [*B*], 1255; *A.*, i, 759.

[6] W. A. Noyes and W. F. Goebel, *J. Amer. Chem. Soc.*, 1922, **44**, 2286; *A.*, 1922, i, 1127.

[7] A. R. Ling and D. R. Nanji, *Biochem. J.*, 1922, **16**, 702; *A.*, 1922, i, 1124; C. A. Brautlecht and N. F. Eberman, *J. Amer. Chem. Soc.*, 1923, **45**, 1934; *A.*, i, 1001.

[8] E. Baur, *Helv. Chim. Acta*, 1922, **5**, 825; *A.*, i, 97.

[9] A. Dorabialski, *Iszy Zjazd Chemików Polskich*, 1923, 25; *A.*, i, 754.

[10] O. W. Snow and J. F. S. Stone, *T.*, 1923, **123**, 1509.

in presence of potassium carbonate with the formation of $\alpha\alpha'$-di-*n*-butoxytrimethylamine, $NMe(CH_2{\cdot}O{\cdot}C_4H_9)_2$, which should prove a useful synthetic agent. Other interesting examples of the preparation [11] of alkylamino-ethers are given by following the same procedure, among which are dimethylaminomethyl *iso*butyl ether, $CHMe_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}NMe_2$, and diethylaminomethyl *n*-butyl ether, $Et_2N{\cdot}CH_2{\cdot}O{\cdot}C_4H_9$. The latter is easily decomposed by water, whereas its methochloride is remarkably stable towards hydrolytic agents. The alkylamino-ethers condense with organomagnesium compounds according to the scheme $R_2N{\cdot}CH_2{\cdot}|O{\cdot}C_4H_9 + R'Mg{\cdot}Hal \longrightarrow R_2N{\cdot}CH_2R' + C_4H_9{\cdot}O{\cdot}Mg{\cdot}Hal$ and with the use of appropriate Grignard reagents prepared from allyl chloride or *iso*amyl bromide the following compounds have been isolated: Δ^{γ}-butenyldiethylamine, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2$; δ-methyl-*n*-amyldiethylamine, $CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2$. The reaction is a valuable one and is general in its application.

The perhalides of the three simplest tetra-alkylammonium halides have been prepared [12] by adding the appropriate halogen in alcohol or acetic acid to a similar solution of the quaternary salt. These products are interesting examples of the multivalent nature of the halogens: NR_4X_3, NR_4X_5, NR_4X_7, NR_4X_9, NR_4X_{13}. Similar examples of perhalides of the phenyltrimethylammonium type are described by another author,[13] and among other properties mentioned, one which was used as a means of determining constitution is of interest. This is the successive detachment of some of the halogens either with acetone or ethyl malonate. These compounds yield halogen on heating and give rise to a salt of the ammonium radical.

An interesting generalisation has been reached with regard to the behaviour of mixed alkyl sulphides towards cyanogen bromide.[14] In the cases which have been studied, the smaller alkyl radical is eliminated as alkyl bromide, whilst the larger one remains associated with sulphur as the thiocyanate, $C_3H_7{\cdot}S{\cdot}C_4H_9 + CNBr \longrightarrow C_3H_7Br + C_4H_9{\cdot}S{\cdot}CN$, but, on the other hand, the benzyl radical is more readily detached from sulphur than the smallest alkyl group. A warning is given against the use of potassium cyanide as a means of preparing allyl cyanide from allyl bromide, since the alkaline nature of this reagent leads [15] to the rapid isomerisation of allyl cyanide to crotononitrile:

$$CH_2{:}CH{\cdot}CH_2{\cdot}CN \longrightarrow CH_3{\cdot}CH{:}CH{\cdot}CN.$$

[11] G. M. Robinson and R. Robinson, *T.*, 1923, **123**, 532.
[12] F. D. Chattaway and G. Hoyle, *ibid.*, p. 654.
[13] H. McCombie and T. H. Reade, *ibid.*, p. 141.
[14] J. von Braun and P. Engelbertz, *Ber.*, 1923, **56**, [*B*], 1573; *A.*, i, 893.
[15] K. von Auwers, *ibid.*, p. 1172; *A.*, i, 661.

The addition of ammonia or alkylamines to allyl cyanide furnishes a ready means to the synthesis of β-aminobutyronitriles. If the alkylamines used contain not more than three carbon atoms, isomerisation occurs into crotononitriles. Reduction of these β-aminonitriles provides an easy route to the αγ-diamino(or alkylamino)-butanes.[16]

A method leading to the synthesis of β-nitroethyl alcohol and its chloroamino-derivatives is worthy of notice, as this interesting compound is now available by a process involving the degradation of nitrotrimethyleneglycol,[17] whilst the synthesis of a number of new aminohydroxy-acids[18] is described either from keto-alcohols by the cyanohydrin method or from olefinecarboxylic acids by the following stages: olefinecarboxylic acid → β-methoxy-α-acetatomercuric ester → β-methoxy-α-bromomercuric ester → α-bromo-β-methoxy-acid → α-amino-β-hydroxy-acid, and the new method will probably prove valuable in the purely aliphatic series.

W. N. Haworth.

Part II.—Homocyclic Division.

Reactions and Preparative Methods.

Reduction.—Numerous special investigations of the scope and mechanism of the process of catalytic hydrogenation are still being prosecuted, whilst the application of the method to the elucidation of structural problems has become a commonplace. Nevertheless, a graded set of standard procedures is as much a *desideratum* as ever, and a close examination of all the operative factors is necessary. For example, it has been shown that, in the hydrogenation of naphthalene in presence of platinum black, the course of the reduction is very much affected by the proportion of oxygen present in the catalyst or the hydrogen employed.[1] In the complete absence of oxygen, the hydrocarbon is not reduced. In presence of the minimum amount of oxygen, the product is tetrahydronaphthalene. If the oxygen is present in small relative amount, the chief product is decahydronaphthalene without detectable intermediate stages, but if the oxygen content of the catalyst is considerable, then the tetrahydro-derivative is again predominatingly produced. The

[16] P. Bruylants, *Bull. Soc. chim. Belg.*, 1923, **32**, 256; *A.*, i, 762.

[17] R. Wilkendorf and M. Trénel, *Ber.*, 1923, **56**, [*B*], 611; *A.*, i, 288.

[18] N. E. Zelinsky and E. F. Dengin, *Ber.*, 1922, **55**, [*B*], 3354; *A.*, 1922, i, 1126.

[1] R. Willstätter and F. Seitz, *Ber.*, 1923, **56**, [*B*], 1388; *A.*, i, 771.

explanation advanced is that spongy platinum poor in oxygen content induces reduction through intermediate phases of relatively small stability, and it is thought that these must include dihydronaphthalenes such as the 1 : 5-isomeride in which the hydrogen is attached to both nuclei. If such highly unsaturated substances have more than a momentary existence, they become perhydrogenated. These unstable dihydronaphthalenes are, however, even more readily dehydrogenated by platinum rich in oxygen and in these circumstances can only be produced in minute amount. The more stable intermediate in the production of tetrahydronaphthalene is thought to be 1 : 2-dihydronaphthalene. It is important to notice that under conditions favourable to the formation of decahydronaphthalene from naphthalene, tetrahydronaphthalene is but slowly reduced. High yields of *ar*-tetrahydro-α-naphthol and α-ketotetrahydronaphthalene from α-naphthol and of *ar*-tetrahydro-α-naphthylamine from α-naphthylamine have been obtained by applications of the Sabatier–Senderens method at temperatures of 100—110° and 135—145°, respectively.[2] The catalytic hydrogenation of phenetidine in the presence of nickel salts and under pressure yields a number of products, of which the chief are the two stereoisomeric 4 : 4′-diethoxyphenyl*cyclo*hexylamines,

$$OEt\cdot C_6H_4\cdot NH\cdot C_6H_{10}\cdot OEt.$$[3]

The stability of the ethoxyl group is interesting, but a more straightforward process is the reduction of *o*- or *p*-aminophenol to respective amino*cyclo*hexanols, which is accomplished in presence of reduced nickel at 180° and 60 kg. pressure.[4] Under the correct conditions, Rosenmund's method of preparation of aldehydes by catalytic reduction of acid chlorides has now been shown to be applicable to unsaturated substances. Thus *o*-chlorocinnamaldehyde is obtained from *o*-chlorocinnamoyl chloride.[5] A process for the preparation of phenylhydrazine which has been patented has some suggestive features. Aniline is diazotised in the presence of an excess of sulphurous acid and the solution reduced at a zinc or tin cathode.[6] It is noteworthy that the action of hot alcoholic potassium hydroxide on benzophenones often effects reduction to the related benzhydrol and particularly that benzhydrol is obtained in this manner from 2-bromobenzophenone. The reaction is

[2] S. Komatsu and R. Nodzu, *Mem. Coll. Sci. Kyoto*, 1923, **6**, 177; *A.*, i, 782.

[3] J. von Braun and E. Hahn, *Ber.*, 1922, **55**, [*B*], 3770; *A.*, i, 102.

[4] J. B. Senderens and J. Aboulenc, *Compt. rend.*, 1923, **177**, 158; *A.*, i, 919.

[5] K. W. Rosenmund, F. Zetzsche, and G. Weiler, *Ber.*, 1923, **56**, [*B*], 1481; *A.*, i, 799.

[6] H. Wachi, Japan Pat. 40194; *A.*, i, 67.

inhibited by the presence of a hydroxyl, ethoxyl, or amino-group in the para-position to the carbonyl.[7]

Oxidation.—The introduction by Gadamer of mercuric acetate as an oxidising agent especially applicable to the removal of hydrogen from hydrogenated heterocyclic bases and alkaloids has provided a valuable resource in a particular field, but apparently lead tetra-acetate has even more useful properties. Indeed, it appears to be unique among oxidising agents, since the characteristic effect is to replace labile hydrogen by the acetoxy-group or to add two such groups to a double bond. Some of the more interesting examples are among aliphatic compounds, but it may be noted here that toluene may be converted into benzyl acetate, diphenylmethane into benzhydryl acetate, and, naturally most readily of all, triphenylmethane into triphenylcarbinyl acetate.[8]

The oxidation of aromatic amines to nitroso- or nitro-compounds by means of monopersulphuric acid or Caro's acid has already proved a serviceable method in the case of nitroamines and has now been applied to the aminoanthraquinones. The 1-aminoanthraquinones yield nitroso-derivatives, whilst 2-nitroanthraquinone is obtained from 2-aminoanthraquinone.[9] This nitroanthraquinone was not previously accessible.

Halogenation.—It has been shown [10] that the simultaneous action of pyridine and bromine on many substances leads to the formation of quaternary pyridinium bromides. Thus quinol yields quinolpyridinium bromide, $C_6H_3(OH)_2 \cdot N(C_5H_5)Br$, by mere treatment in pyridine solution at a low temperature with a molecular proportion of bromine, also dissolved in pyridine. Under different conditions, pyridine or quinoline may be employed to effect a control of bromination either in addition or substitution. The most certain method is to employ ready-formed quinoline dibromide hydrobromide as the brominating agent in acetic acid solution, but it usually suffices to add the calculated amount of bromine solution from a burette to a solution of the substance and of a mineral acid salt of pyridine or quinoline in acetic acid. The termination of the reaction is indicated by the production of a yellow coloration due to the presence of the dibromide hydrobromide. The normal dibromide of safrole was readily obtained in this way and the preparation of mono- and di-bromo-

[7] P. J. Montagne, *Rec. trav. chim.*, 1920, **39**, 339; 1922, **41**, 703; 1923, **42**, 499; *A.*, 1920, i, 394; 1923, i, 227, 801.

[8] O. Dimroth and R. Schweizer, *Ber.*, 1923, **56**, [*B*], 1375; *A.*, i, 744.

[9] E. Kopetschni, D.R.-P. 363930; from *Chem. Zentr.*, 1923, ii, 1029; *A.*, i, 1021.

[10] E. de B. Barnett, J. W. Cook, and E. P. Driscoll, *T.*, 1923, **123**, 503.

pyrogallols, monobromocatechol, and bromotyrosine presented no difficulty.[11]

Decompositions.—The formation of lactones by the action of iodine on the silver salts of substituted glutaric acids has been studied in the alicyclic series. The normal case is illustrated by the following example :

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2Ag\\CH_2\cdot CO_2Ag\end{matrix}\xrightarrow{+I_2}CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot O\\CH_2\cdot CO\end{matrix}+2AgI+CO_2.$$

Silver *cis*-hexahydrohomophthalate yields hexahydrophthalide, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH_2\\CH_2\cdot CH_2\cdot CH\text{—}CO\end{matrix}>O$, and it is interesting that the same substance is obtained, although in smaller yield, by the action of iodine on the silver salt of the *trans*-acid. Silver *cis*-hexahydro*iso*phthalate undergoes the reaction, but a remarkable exception has been found in silver camphorate, which is changed by iodine into camphoric anhydride.[12] The cherished belief that alkali metals are inactive towards ethers must now be somewhat modified. Diphenyl ether reacts exothermally with sodium at 180—200°, with formation of phenol and benzene, together with small relative amounts of diphenyl and products of higher molecular weight. The ethyl ethers of phenol and the naphthols are similarly decomposed above 200°, whilst benzyl ethyl ether reacts with sodium at 140°.[13]

Another investigation has brought to light still more striking phenomena of a similar type. The ethers having the formulæ $Ph_2C{:}CH\cdot CPh_2\cdot OEt$, $CPh_3\cdot OEt$, $CPh_3\cdot OPh$, $CHPh_2\cdot OEt$, $CHPh_2\cdot O\cdot CHPh_2$, $Ph_2C(OMe)_2$, $CPh_3\cdot SPh$, are all decomposed when shaken in cold anhydrous ethereal solution with potassium powder or sodium-potassium alloy in the sense of the equation

$$R\cdot O\cdot R' + 2K = RK + KOR'.$$[14]

Quite unexpectedly it was found that the isomeric hydrocarbons $CHPh_2\cdot CHPh_2$ and $CPh_3\cdot CH_2Ph$ suffer fission in similar circumstances, although they are stable individuals exhibiting no tendency to dissociate. The disruption of the bond by the alkali metal is attributed to its character as a weakened valency. Fundamentally, an alkali metal must be regarded as a donator of electrons, and in the reporter's view the occurrence of the reaction shows that

[11] K. W. Rosenmund and W. Kuhnhenn, *Ber.*, 1923, **56**, [*B*], 1262; *A.*, i, 782; K. W. Rosenmund, W. Kuhnhenn, and W. Lesch, *ibid.*, p. 2042; *A.*, i, 1095.

[12] A. Windaus, F. Klänhardt, and G. Reverey, *Ber.*, 1922, **55**, [*B*], 3981; *A.*, i, 111; M. Bredt-Savelsberg, *J. pr. Chem.*, 1922, [ii], **105**, 149; *A.*, i, 1097.

[13] P. Schorigin, *Ber.*, 1923, **56**, [*B*], 176; *A.*, i, 207.

[14] K. Ziegler and F. Thielmann, *ibid.*, p. 1740; *A.*, i, 921.

the carbon atom which becomes separated from oxygen is one which has a tendency to acquire an electron. This tendency is due in most of the above examples to its union with the key-positive phenyl groups. From this standpoint the fission and reduction of *s*-tetraphenylethane by potassium is correlated with the fact that tetraphenylethylene is readily reducible but difficult to oxidise or brominate. Alkyl groups are key-negative and tetramethylethylene is difficult to reduce, but absorbs bromine with avidity. In this case, the unsaturated carbon atoms tend, not to acquire, but to give up electrons. The reversibility of the benzoin condensation has been experimentally proved. The equilibrium constant between benzaldehyde and benzoin at 79° in 95 per cent. alcohol in presence of sodium cyanide is about 0·245.[15] Closely related is the observation that benzil, furil, anisil, and piperil may be readily ammonolysed under the influence of ammonium cyanide.[16] Thus benzil is practically quantitatively converted into benzamide and benzaldehydecyanohydrin.

Condensations and Additive Syntheses.—Brief reference may be made to the fact that Tollens's well-known synthesis of polyhydroxy-compounds by the action of excess of formaldehyde on ketones or aldehydes in the presence of calcium hydroxide has been extended to cyclic ketones. According to the conditions, *cyclo*hexanone yields either 2 : 2 : 6 : 6-tetrahydroxytetramethyl*cyclo*hexan-1-ol,

$$(CH_2{\cdot}OH)_2{\cdot}C{\cdot}CH(OH){\cdot}C(CH_2{\cdot}OH)_2$$
$$CH_2{\cdot}CH_2{-}CH_2$$

or acetals derived by further condensation with formaldehyde. With limited amounts of formaldehyde, it is possible to obtain the keto-alcohols. *cyclo*Pentanone with much formaldehyde yields insoluble amorphous products and with 4—6 molecular proportions it is converted into 2 : 2 : 5 : 5-tetrahydroxytetramethyl*cyclo*pentan-1-one. This substance is unchanged by reagents for the carbonyl group, but its bismethylene ether can be reduced to a secondary alcohol. Menthone, carvone, and camphor are inactive towards formaldehyde.[17] The condensation of aldehydes with substances containing the group $-CH_2-CO-$ in presence of alkaline catalysts is one of the most useful of synthetical methods, but in many cases it is difficult to devise a suitable means of protection of phenolic hydroxyl groups the presence of which frequently involves a tendency of the products to resinify. It is now suggested that

[15] E. Anderson and R. A. Jacobson, *J. Amer. Chem. Soc.*, 1923, **45**, 836; *A.*, i, 467.

[16] H. D. Dakin and C. R. Harington, *J. Biol. Chem.*, 1923, **55**, 487; *A.*, i, 583; compare A. Lachman, *J. Amer. Chem. Soc.*, 1923, **45**, 1522; *A.*, i, 785.

[17] C. Mannich and W. Brose, *Ber.*, 1923, **56**, [*B*], 833; *A.*, i, 565.

the methoxymethyl group may serve the purpose, and *o*-cumaraldehyde, for example, is prepared by condensing *o*-methoxymethoxybenzaldehyde with acetaldehyde in the usual manner followed by a short hydrolysis with boiling 50 per cent. acetic acid containing 0·3 per cent. of sulphuric acid.[18] In the course of an examination of cymene derived from different sources, it has been incidentally noted that the " cymene " prepared from toluene and *iso*propyl bromide with the help of aluminium chloride is a meta-compound.[19] Thymol is said to be obtained in satisfactory yield by hydrolysis with superheated steam of the sulphonated thymol which is the product of the condensation of polysulphonated *m*-cresol and *iso*propyl alcohol in sulphuric acid solution at 90°.[20] The use of a halogenalkyl toluene-*p*-sulphonate for the introduction of halogenalkyl groups into phenols and amines was noted last year,[21] and it has now been found that towards the Grignard reagent also the sulphonic ester group is more reactive than the halogen.[22] An example is the production in 75 per cent. yield of β-chloroethylphenylacetylene, $CH_2Cl{\cdot}CH_2{\cdot}C{:}CPh$, from $CH_2Cl{\cdot}CH_2{\cdot}O{\cdot}SO_2{\cdot}C_7H_7$ and $CPh{:}C{\cdot}MgBr$. Unsymmetrically substituted benzoins may be prepared [23] by taking advantage of the interaction of aromatic aldehydecyanohydrins and aryl magnesium salts in ethereal solution. The process gives moderate yields, and may even be applied to the production of *o*-hydroxybenzoin from salicylaldehydecyanohydrin and magnesium phenyl bromide. Furfuraldehydecyanohydrin and magnesium phenyl bromide yield *iso*benzfuroin,

$$C_4H_6O{\cdot}CH(OH){\cdot}\dot{C}OPh,$$

which is stated to be not identical with E. Fischer's benzfuroin.[24] The latter must therefore have the constitution $C_4H_6O{\cdot}CO{\cdot}CHPh{\cdot}OH$, and if these individuals or a similar pair can really be isolated in such a simple manner in a pure condition, a study of their equilibrium in presence of alkali should prove of much interest. The chemistry of the indones has been little investigated, largely, no doubt, because these substances are not very readily accessible. 2 : 3-Diphenylindone is obtained in 89 per cent. yield when the dibromide of benzylidenedeoxybenzoin is heated at 140—145°.[25]

[18] H. Pauly and K. Wäscher, *Ber.*, 1923, **56**, [*B*], 603; *A.*, i, 342.

[19] K. von Auwers and H. Kolligs, *Ber.*, 1922, **55**, [*B*], 3872; *A.*, i, 99.

[20] Howard & Sons, Ltd., and J. W. Blagden, Brit. Pat. 1923, 197848; A., i, 781.

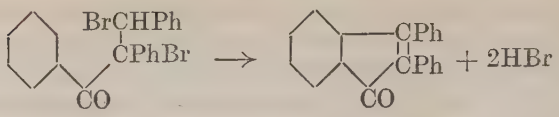
[21] *Annual Reports*, 1922, 93.

[22] H. Gilman and N. J. Beaber, *J. Amer. Chem. Soc.*, 1923, **45**, 839; *A.*, i, 453.

[23] Y. Asahina and M. Terasaka, *J. Pharm. Soc. Japan*, 1923, No. **494**, 219; *A.*, i, 1023.

[24] E. Fischer, *Annalen*, 1882, **211**, 288.

[25] A. P. Orékhov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1827; *A.*, i, 454.



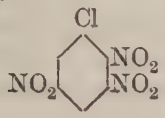
Diazotisation.—In presence of a large excess of aqueous hydrochloric acid and nitrous acid, triaminomesitylene suffers twofold diazotisation, and the product was isolated as aminomesitylene-bisdiazonium chloroaurate.[26] This interesting result renders it probable that under ordinary conditions not more than two amino-groups attached to one and the same benzene ring can be diazotised. It may mean that the benzene ring cannot carry more than two diazonium groups, and this is the emphatic opinion of the authors. Apparently the only alternative explanation is that the direct attachment of two *onium* groups to the nucleus distributes a positive charge which inhibits the amino-group from attracting a proton.

Substitution and Orientation.

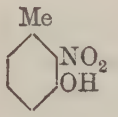
In connexion with the theory of Reddelien that substitution in aromatic compounds is preceded by the formation of additive products, it is of interest to note that a mixture of the composition $PhNO_2,H_2SO_4$ slowly crystallises, when cooled to $-10°$ to $-20°$, in pale green needles, m. p. 11°. The substance is sufficiently stable to be capable of crystallisation from an ethereal solution.[27] From observations of the electrical conductivity of sulphuric acid solutions, it is concluded that *p*-nitrotoluene is about half as strong a base as 2 : 4-dinitroaniline. Dinitro-compounds are not basic and when added to sulphuric acid diminish its electrical conductivity. A careful examination of the products of nitration of benzaldehyde by the method of thermal analysis has been made.[28] About 19 per cent. of the product is *o*-nitrobenzaldehyde and this accords closely with the conclusions previously derived, in all probability, from works practice in the manufacture of Patent Blues. The nitration of *p*-fluorobenzoic acid yields, to the extent of 80 per cent., 4-fluoro-3-nitrobenzoic acid, but *p*-fluoronitrobenzene is also formed.[29] The fluorine atom accordingly finds a place among the groups which have a sufficiently powerful directive influence to induce displacement. The difficulty of achieving consistency in the interpretation of orientation results among complex benzene derivatives is well illustrated by the outcome of a research on the

[26] G. T. Morgan and G. R. Davies, *T.*, 1923, **123**, 228.
[27] É. Cherbuliez, *Helv. Chim. Acta*, 1923, **6**, 281; *A.*, i, 452.
[28] O. L. Brady and S. Harris, *T.*, 1923, **123**, 484.
[29] H. Rouche, *Bull. Acad. roy. Belg.*, 1921, 534; *A.*, i, 214.

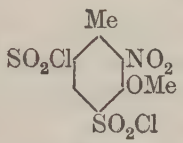
nitration and bromination of 2 : 3-dialkyloxybenzaldehydes.[30] Bromination is found consistently to occur in position 5, but nitration occurs in positions 5 and 6 in the 2-ethoxy-3-methoxy-derivatives and in position 6 in the case of 2 : 3-dimethoxybenzaldehyde.[31] Another difficult case is furnished by the nitration of 2 : 3-dinitrochlorobenzene,[32] which yields a considerable proportion of 2 : 3 : 5-trinitrochlorobenzene (I). There is evidently some overlapping in the operation of the various factors controlling orientation, and we are not yet in a position usefully to discuss these examples. The nitration of sulphonated *m*-cresol gives a product which yields 2-nitro-*m*-cresol (II) on hydrolysis,[33] or 3-methoxytoluene-4 : 6-disulphonyl chloride may be converted into the 2-nitro-derivative (III) and then into 2-nitro-*m*-cresol by hydrolysis with acids or alkalis.[34]



(I.)



(II.)



(III.)

The latter device, which was elaborated in connexion with work on the preparation of the four isomeric *m*-tolyl methyl ether sulphonic acids, may frequently prove serviceable in attempts to introduce substituents in unusual or unfavoured positions. Some further observations in connexion with phenols may now be reviewed. The existence of the so-called " di-iodophenol iodide " [35] obtained by the action of iodine on an alkaline solution of phenol has been repeatedly denied,[36] but is now reaffirmed.[37] The substance occurs in dark violet-brown leaflets, m. p. 122°, and is best obtained by the prolonged action of cold sodium hypoiodite on phenol. A by-product is tetraiododiphenylenequinone,

$$O{:}C_6H_2I_2{:}C_6H_2I_2{:}O$$

(Lautemann's red), and the same two substances are said to be obtained by the oxidation of tri-iodophenol by means of potassium persulphate in presence of sodium carbonate. The perplexing

[30] W. Davies, *T.*, 1923, **123**, 1575; W. Davies and L. Rubenstein, *ibid.*, p. 2839.

[31] W. H. Perkin and R. Robinson, *T.*, 1914, **105**, 2389.

[32] A. F. Hollemann, *Proc. Acad. Amsterdam*, 1922, **25**, 223; *Chem. Abstr.*, 1922, **16**, 4193.

[33] G. P. Gibson, *T.*, 1923, **123**, 1269.

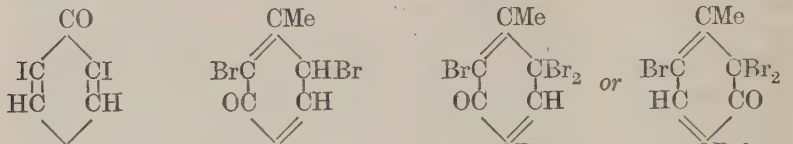
[34] R. D. Haworth and A. Lapworth, *T.*, 1923, **123**, 2982.

[35] Messinger and Vortmann, *A.*, 1890, 1473.

[36] Bougault, *A.*, 1908, ii, 738; Wilkie, *A.*, 1911, ii, 546; 1912, i, 346; Hunter and Woollett, *A.*, 1921, i, 238.

[37] G. Vortmann, *Ber.*, 1923, **56**, [*B*], 234; *A.*, i, 206.

feature is that the constitution (IV) assigned to "di-iodophenol iodide" is that of a tautomeric form of tri-iodophenol. This seems highly improbable, and if the substance exists it must surely have two iodine atoms on one of the carbon atoms in the *o*- or *p*-positions so as to give it blocked hydroaromatic character. In the case of the action of bromine or hypobromites on thymol, a similar matter has been cleared up during the past year.



(IV.) (V.) (VI.)

The product to which the formula (V) had been assigned[38] proves to be impure dibromothymol, and its partial insolubility in solutions of alkali hydroxide was due to admixture with tribromo-*p*-menthadienone (VI), which is best prepared by the action of calcium bromohypobromite on thymol in aqueous solution.[39] It has been found that *C*-alkylation of phenols is the rule rather than the exception when alkyl halides and the sodium derivatives of phenols are allowed to interact at elevated temperatures in non-dissociating solvents, for example, in benzene or toluene.[40] A note of caution must be sounded, because the groups which have been introduced are allyl, benzyl, and cinnamyl, which are of a special type. The substitution occurs preferentially in the ortho-position. As an example, phenyl cinnamyl ether is obtainable from cinnamyl bromide and sodium phenoxide in alcoholic solution, but in benzene, *o*-cinnamylphenol is exclusively formed. It is interesting to note that the phenyl ethers of *o*- or *p*-nitrated phenols are more reactive than the alkyl ethers.[41]

β-2 : 4-Dinitrophenylhydroxylamine, $(NO_2)_2C_6H_3{\cdot}NH{\cdot}OH$, can be obtained by the action of hydroxylamine in alcoholic solution on 2 : 4-dinitrodiphenyl ether.[42] It has marked acidic properties and forms intensely coloured ammonium and phenylammonium salts. There has been much activity in the development of the chemistry of the simpler naphthalene derivatives, but no orientation rules in this series have yet been propounded which will satisfy all or nearly all the requirements. The suggestion that directive substituents

[38] Dannenberg, *A.*, 1903, i, 338.

[39] H. Jost and F. Richter, *Ber.*, 1923, **56**, [*B*], 119; *A.*, i, 208; compare Crowther and McCombie, *T.*, 1913, **103**, 539.

[40] L. Claisen, *Z. angew. Chem.*, 1923, **36**, 478; *A.*, i, 1094.

[41] W. Borsche, *Ber.*, 1923, **56**, [*B*], 1488; *A.*, i, 780.

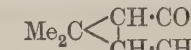
[42] *Ibid.*, p. 1494; *A.*, i, 778.

should be divided into a quinonoid type (*o*-, *p*-) and a non-quinonoid type (*m*-) [43] leads to exactly the same results as the theory of induced alternate polarities, but presents no special advantages. It is the effect of the fusion of the rings which remains ambiguous, apart from the obvious enhancement of the reactivity of the α-positions which reaches the maximum in the 9- and 10-positions in anthracene. A monosubstituted naphthalene is analogous to a trisubstituted benzene, and the material necessary for a complete solution of the orientation problem is not yet at our disposal in either case. A careful re-examination [44] of the sulphonation of naphthalene has shown *inter alia* that at higher temperatures, for example at 180°, the disulphonic acid predominatingly formed is the 2 : 7-isomeride, and not the 2 : 6 as at present believed. The latter acid is stated to yield a sparingly soluble anhydride on heating with water at 135° in a closed vessel. A reaction new to the naphthalene series is the formation of a diazonium compound of the probable constitution $HO{\cdot}C_{10}H_5{<}^{N_2}_{SO_3}$ by the action of nitrous acid on a solution of naphthalene-2-sulphonic acid in sulphuric acid containing a trace of mercuric oxide or selenium. The benzene orientation rules as interpreted in terms of the polarity theories are followed in the bromination of 2-nitronaphthalene to the 5-bromo-derivative [45] (in the corresponding nitration position 8 also is attacked) and in the nitration of aceto-β-naphthalide in glacial acetic acid solution, when the nitroxyl enters in the first place the 1-, 8-, or 6-position in order of importance.[46] 3-Nitro-aceto-β-naphthalide has not been found among the products of the reaction. A number of new hydroxynaphthoic acids have been obtained, and in the course of the work the literature has been somewhat extensively revised. The sulphonation of α-naphthoic acid with 98 per cent. sulphuric acid at 100° gives a mixture of the 5-, 6-, and 7-sulpho-α-naphthoic acids.[47] Under similar conditions, β-naphthoic acid yields 5-, 7-, and 8-sulpho-β-naphthoic acids, the former in largest relative amount. At 160°, 7-sulpho-β-naphthoic acid is the main product.[48] Clearly the relatively weak carboxyl group does not exert a very decided orientating influence. The various sulphonaphthoic acids are best obtained from α- and β-naphthylaminesulphonic acids by means of the Sandmeyer reaction.

[43] V. Veselý and M. Jakeš, *Bull. Soc. chim.*, 1923, [iv], **33**, 955; *A.*, i, 911.
[44] H. E. Fierz-David, *J. Soc. Chem. Ind.*, 1923, **42**, 421T; *A.*, i, 1190.
[45] V. Veselý and M. Jakeš, *Bull. Soc. chim.*, 1923, [iv], **33**, 952; *A.*, i, 911.
[46] *Ibid.*, p. 942; *A.*, i, 918.
[47] F. A. Royle and J. A. Schedler, *T.*, 1923, **123**, 1641.
[48] C. Butler and F. A. Royle, *ibid.*, p. 1649.

Natural Products.

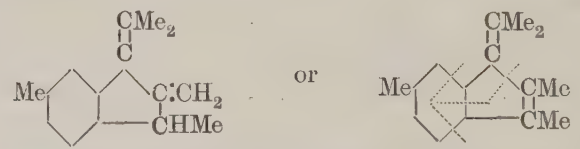
Chrysanthemum cinerariæfolium contains an insecticidal principle which is called "pyrethron." Higher alcohols, an oily substance, and a solid and a liquid acid may be obtained from it, whilst an ester prepared from the liquid acid and the oily substance has the insecticidal properties of the original material. This liquid acid, termed *pyrethronic acid*, has the remarkable constitution



[49]

When reduced with hydrogen in presence of platinum black, it yields a dihydro-derivative, and the glycol obtained by the action of permanganate may be further oxidised to *trans*-caronic acid by means of chromic acid. Ozonisation of the acid yielded caronic acid and its semialdehyde, propionic acid, and propaldehyde. Oil of milfoil contains a curious hydrocarbon, *azulene*, $C_{15}H_{18}$, which apparently yields a sodio-derivative.[50] Catalytic reduction produces a dicyclic hydrocarbon, $C_{15}H_{28}$, and oxidation by means of alkaline permanganate leads to the formation of acetone and (probably) methylphthalic acid.

The annexed formulæ are provisionally suggested and, as indicated by the dotted lines, these may be derived in skeleton from three isoprene units.



The constitution of capsaicin has now been completely elucidated. It will be recalled that the substance has been proved to be the vanillylamide of a decenoic acid and the ambiguity was in connexion with the constitution of the acid fragment. Catalytic reduction of capsaicin yields dihydrocapsaicin, which is as pungent as the original substance. Dihydrocapsaicin is identical with η-methylnonovanillylamide prepared synthetically. This fixes the carbon skeleton and the position of the double bond follows from the oxidation of the decenoic acid by means of potassium permanganate to *iso*butyric and adipic acids.[51] Capsaicin is therefore η-methyl-Δ^{ϵ}-nonenovanillylamide,

$$CHMe_2{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_3{\cdot}(OH){\cdot}OMe.$$

Taxine, a constituent of the yew, *Taxus baccata*, readily yields

[49] R. Yamamoto, *J. Chem. Soc. Japan*, 1923, **44**, 311; *A.*, i, 1010; compare *A.*, 1919, i, 465.

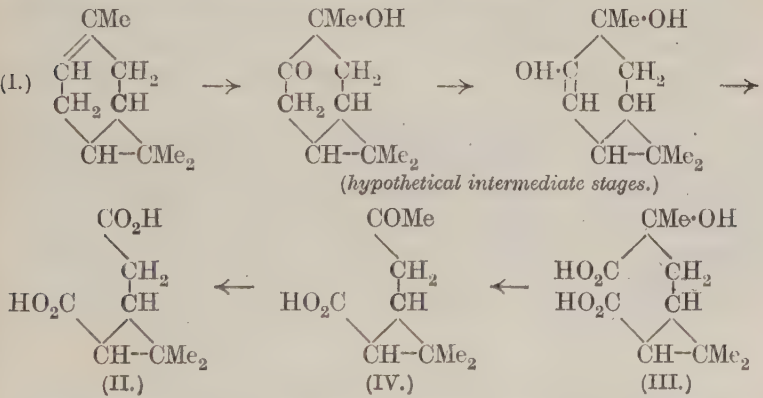
[50] R. E. Kremers, *J. Amer. Chem. Soc.*, 1923, **45**, 717; *A.*, i, 454.

[51] E. K. Nelson and L. E. Dawson, *ibid.*, p., 2179; *A.*, i, 1108.

cinnamic acid in several ways and its behaviour is expressed by the following provisional formula :

$$NMe_2 \cdot CHPh \cdot CH_2 \cdot CO_2 \cdot C_{24}H_{34}O_6 \cdot OAc.$$[52]

The oxidation of the terpene derived from Indian turpentine (*ex Pinus longifolia*, Roxb.) by means of potassium permanganate in acetone solution has furnished results which go far to justify the assignment of the *d*-Δ^3-carene structure (I) to it.[53] The more important products are *cis*- and *trans*-caronic acids, a dibasic acid, $C_8H_{12}O_4$, probably *cis*-homocaronic acid (II), and two dibasic hydroxy-acids, $C_{10}H_{16}O_5$ (III), which are α-hydroxy-acids, and by further oxidation yield isomeric keto-acids, $C_9H_{14}O_3$ (IV). In view of the simultaneous formation of *cis*- and *trans*-caronic acids there can be little doubt that the isomerism of the pairs of acids $C_{10}H_{16}O_5$ and $C_9H_{14}O_3$ is also stereochemical. Only one of the keto-acids was obtained in sufficient quantity to demonstrate that it is a methyl ketone. On treatment with alkaline hypobromite, bromoform and the acid (II) were obtained. The course of the degradation is shown in the following scheme :



The higher-boiling fractions of this variety of Indian turpentine contain a sesquiterpene, *d*-longifolene, which possesses a stable molecular structure very difficult to break up.[54] It is almost inert towards potassium permanganate, but may be oxidised by means of chromic acid with formation of longifolic acid and, under some conditions, *iso*longifolic acid, $C_{14}H_{22}O_2$, as well as an α-diketone, $C_{15}H_{22}O_2$, to which the not very euphonious name *d*-longif-1 : 2-dione has been assigned. Longifolic acid is extremely

[52] E. Winterstein and A. Guyer, *Z. physiol. Chem.*, 1923, **128**, 175; *A.*, i, 942; compare *A.*, 1922, i, 572.

[53] J. L. Simonsen and M. G. Rau, *T.*, 1923, **123**, 549; cf. J. L. Simonsen, *Indian Forest Records*, 1923, **10**, iv, for occurrence of *d*-Δ^3-carene in the essential oil from the oleo-resin of *Pinus Merkusii*.

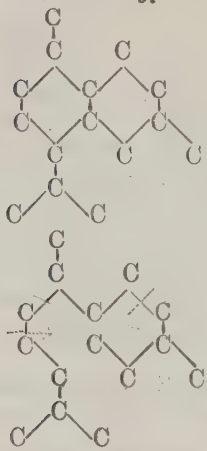
[54] J. L. Simonsen, *T.*, 1923, **123**, 2642.

stable, certainly saturated, and therefore tricyclic. Longifdione yields a quinoxaline, a monoxime, and similar derivatives and is oxidised by a mixture of nitric and sulphuric acids to a dibasic acid, $C_{15}H_{24}O_4$, which yields an anhydride. The simultaneous formation and the properties of longifolic acid and longifdione cannot be explained on any simple hypothesis, and in the absence of further information structural speculations are premature.

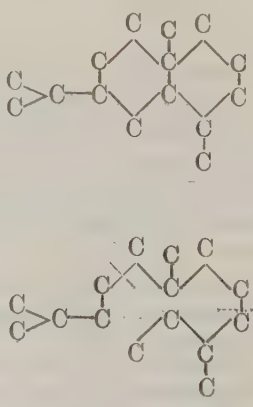
On dehydrogenation with sulphur, many sesquiterpenes yield the hydrocarbon *cadalene*, which has already been proved to be 4 : 7-dimethyl-1-*iso*propylnaphthalene, but another group of the hydrocarbons on similar treatment gives *eudalene*, a methyl*iso*propylnaphthalene not identical with any of the *apo*cadalenes. Eudalene has now proved to be 1-methyl-7-*iso*propylnaphthalene and has been synthesised [55] by a method which need not be detailed, as it is similar to that used in the case of cadalene.[56]

In order to develop the sesquiterpene skeleton from that of eudalene, it is necessary to introduce one more carbon atom in such a position that the group containing it must be ejected when a naphthalene derivative is formed. If the further condition be added that the structure must be divisible into isoprene units, there is only one solution, which is shown below under the heading "eudesmol type." It is instructive to note how the skeletons of each of the classes of hydronaphthalenoid sesquiterpenes contain the three-isoprene chain of farnesol. The head to tail union of isoprene residues which is characteristic of the aliphatic terpenes is repeated. It is curious that both the cadinene and eudesmol skeletons can be opened in two ways so as to give the farnesol chain, but only one of these is indicated.

Cadinene type.

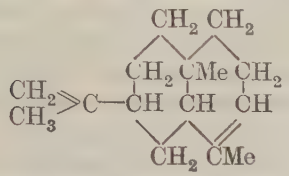


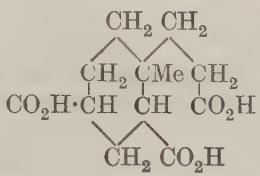
Eudesmol type.



[55] L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1922, 5, 923; *A.*, i, 119.
[56] *Ann. Reports*, 1922, 118.

The constitution IV is assigned to α-selinene, which on oxidation yields a tricarboxylic acid (V).[57] The fact that the latter can be readily esterified and the ester hydrolysed is held to prove that the carboxyl groups are not attached to tertiary carbon atoms, and in that case the eudesmol-type skeleton receives experimental support.

(IV.) 

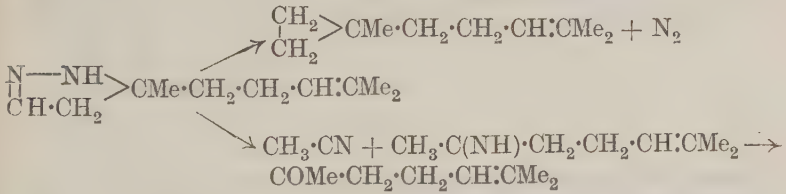
 (V.)

The chemistry of pimaric and abietic acids is being actively pursued, but the results are not yet such as can be usefully reported in detail.

A crystalline *dimethyl shellolate*, $C_{17}H_{24}O_6$, is obtained by esterification of the resin acids of shellac,[58] but beyond the fact that shellolic acid is dibasic and contains two hydroxyl groups and a double bond, few facts are known which can be brought to bear on the question of its constitution.

Ring Closure, Alicyclic groups.

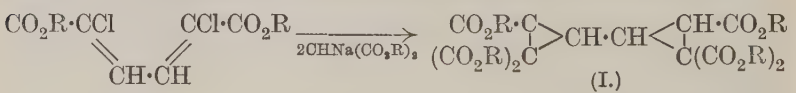
Although citral is an αβ-unsaturated aldehyde, it yields a hydrazone which is semi-stable, being converted into citralpyrazolone only on distillation.[59] This pyrazolone yields *p*-cymene of a high degree of purity when it is heated with fuming hydrochloric acid in a sealed tube. On distillation over alkali hydroxide in presence of platinum, the pyrazolone decomposes as shown in the annexed scheme :



An attempt to prepare methylene*cyclo*propane by the thermal decomposition of *cyclo*propylmethyltrimethylammonium hydroxide, $CH_2{<}_{CH_2}{>}CH{\cdot}CH_2{\cdot}NMe_3{\cdot}OH$, led mainly to the production of *cyclo*propylmethyldimethylamine. Under favourable conditions, the yield of hydrocarbons was about 6·5 per cent., and after the gases

[57] L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1923, **6**, 846; *A.*, i, 1216.
[58] C. Harries and W. Nagel, *Ber.*, 1922, **55**, [*B*], 3833; *A.*, i, 120.
[59] N. Kishner, *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 1; *A.*, i, 385.

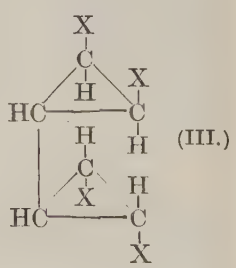
were treated with bromine methylene*cyclo*propane dibromide and a larger relative amount of the tetrabromide of butadiene could be separated.[60] Posthumous honours are to be paid to the Ladenburg "prism" benzene formula, since an attempt to synthesise substances containing this particular "caged" ring system is in progress.[61] There are numerous alternatives in connexion with the order of ring-closure, and the most promising of these involves the production of *cyclo*propyl*cyclo*propane derivatives. An ingenious method has been elaborated whereby suitable compounds of this type become moderately accessible. A re-examination of the products of the action of six molecular proportions of phosphorus pentachloride on mucic acid led to the isolation of the stereoisomeric methyl and ethyl esters of $\alpha\alpha'$-dichloromuconic acid, two in each case, in much improved total yield.[62] These esters react with ethyl sodiomalonate as shown in the following scheme, the stereoisomerides giving identical solid products.



(I.)

The hexacarboxylic ester (I) yields on hydrolysis with alkali a crystalline sodium salt from which the hexacarboxylic acid is readily obtained. The decomposition of the malonic acid groupings proved difficult, but the tetracarboxylic acid (II) has nevertheless been obtained in a pure condition.

(II.)



(III.)

Before the later stages can be attempted, an investigation of the stereochemistry of this acid is necessary, the form III being that which should be most readily convertible into the "caged" system.

The camphor mine still proves inexhaustible and attention may be drawn to the following investigations, the results of which cannot be given in detail: Preparation of a ring homologue of cam-

[60] N. J. Demjanov and M. Dojarenko, *Ber.*, 1923, **56**, [*B*], 2208; *A.*, i, 1192.
[61] E. H. Farmer, *T.*, 1923, **123**, 3332.
[62] *Ibid.*, p. 2531.

phenilone,[63] of 6-methylcamphor and its derivatives,[64] and of phenyl-*apo*camphor.[65]

A passing reference must also be made to the careful work which has been carried out on the stereoisomeric pinanes.[66]

Optically homogeneous *l*-pinene yields on hydrogenation the pure hydrocarbon *pinane*, but impure *d*-pinene or *r*-pinene yields a mixture.

The pure stereoisomeride, termed *pinocamphane*, is obtained from *d*-pinene by way of pinocamphone, the hydrazone of which is heated with alkali hydroxide. A number of investigations converge on the formation of derivatives of 1-ketotetrahydronaphthalene from γ-aryl-*n*-butyric acids. When phenylbutyryl chloride is treated with aluminium chloride according to the method of Kipping and Hill,[67] the yield is said to be only about 10 per cent. of that theoretically possible. When a methyl group is present in varied positions, the yield rises to 70—76 per cent.[68]

At 100°, the dehydration of phenylbutyric acid may be accomplished by sulphuric acid, the yield being about 50 per cent. of the theoretical.[69] The reaction does not occur in this example at the ordinary temperature, and a systematic survey [70] has shown that 1-ketotetrahydronaphthalene derivatives are produced by the action of cold concentrated sulphuric acid only on those γ-phenylbutyric acid derivatives which bear a substituent in the β-position and in addition contain a second carboxyl group. It is suggested that an anhydride is first formed, and that this reacts with sulphuric acid so as to give a mixed anhydride of the carboxylic acid and sulphuric acid, the process being completed by the elimination of sulphuric acid. Alternatively, the nuclear hydrogen may migrate to the carbonyl group of the anhydride.

Although the *cyclo*heptane ring is not distinguished by its ease of formation, it would appear that the structure, once formed, is relatively unstrained. *trans-cyclo*Heptane*spirocyclo*propane-2 : 3-dicarboxylic acid (IV), in respect of its stability to mineral acid, stands intermediate between the related compounds derived from *cyclo*pentane and *cyclo*hexane.[71]

[63] P. Lipp, *J. pr. Chem.*, 1922, [ii], **105**, 50; *A.*, i, 1105.

[64] S. S. Nametkin and (Mlle) A. M. Chuchrikova, *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 254; *A.*, i, 586.

[65] M. Bredt-Savelsberg, *Ber.*, 1923, **56**, [*B*], 554; *A.*, i, 348.

[66] S. S. Nametkin, *J. Russ. Phys. Chem. Soc.*, 1922, **54**, 177; *A.*, i, 811; A. Lipp, *Ber.*, 1923, **56**, [*B*], 2098; *A.*, i, 1214.

[67] *T.*, 1899, **75**, 144.

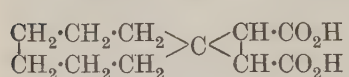
[68] F. Mayer and G. Stamm, *Ber.*, 1923, **56**, [*B*], 1424; *A.*, i, 802.

[69] F. Krollpfeiffer and W. Schäfer, *ibid.*, p. 620; *A.*, i, 343.

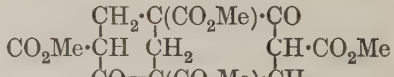
[70] A. J. Attwood, A. Stevenson, and J. F. Thorpe, *T.*, 1923, **123**, 1755.

[71] J. W. Baker and C. K. Ingold, *ibid.*, p. 122.

It is the *cyclo*propane ring which is affected, and the results are interpreted in accordance with the theory of the effect of attached groups on carbon-to-carbon valencies to which reference has been made in previous reports. The conclusion that the *cyclo*heptane ring is unstrained, and therefore in all probability lies in more than one plane, has also been reached from the observation of the close relation of a representative of the series with a *tricyclo*nonane derivative. When set up on the models, the *tricyclo*nonane structure is seen to be almost necessarily stable and free from valency strain, and it is argued that the ready formation of the simpler ring-system from it shows that this also must be free from strain. Whatever may be thought of the validity of this reasoning, there can be no doubt in regard to the great interest of the investigation now under discussion.[72] Any one of the products obtained by the condensation of formaldehyde and methyl malonate yields more or less methyl *dicyclo*-[1, 3, 3]-nonane-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate (V) when boiled with concentrated methyl-alcoholic sodium methoxide.[73] The best results are obtained by using a mixture of methyl methylenebismalonate (1 mol.) and methyl methylenemalonate (2 mols.).



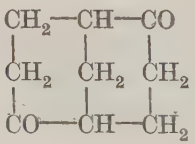
(IV.)

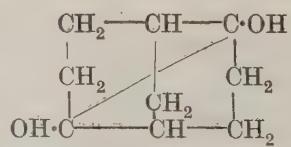


(V.)

The tetracarboxylic ester yields *dicyclo*nonanedione (VI) on hydrolysis by means of hot dilute hydrochloric acid. The disemicarbazone of this diketone is converted by 10 per cent. ethyl-alcoholic sodium ethoxide solution at 220° into dicyclo*nonane*, which occurs in feathery, plastic crystals melting at 145—146°. Reduction of *dicyclo*nonanedione with sodium amalgam produces the corresponding disecondary alcohol and the pinacol (VII), which is a *tricyclo*nonane derivative and belongs to the "caged" ring type of associated cyclic systems.

(VI.)



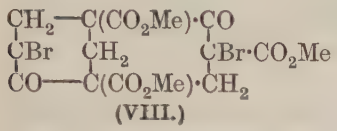


(VII.)

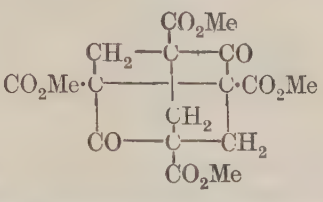
[72] H. Meerwein, F. Kiel, G. Klösgen, and E. Schoch, *J. pr. Chem.*, 1922, [ii], **104**, 161; *A.*, i, 221.

[73] H. Meerwein and W. Schürmann, *Annalen*, 1913, **398**, 196; *A.*, 1913, i, 869.

The tetracarboxylate (V) yields a disodio-derivative which reacts with bromine (5 atoms) to give methyl dibromo*dicyclo*nonanedione-tetracarboxylate (VIII). It is very noteworthy that this substance melts at 142° with elimination of bromine and production of methyl *tricyclo*nonanedionetetracarboxylate (IX).



(VIII.)



(IX.)

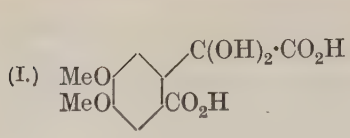
The *tricyclo*-ester is also obtained by the thermal decomposition of the copper derivative of V and in several other ways, best of all by treatment of the monobromo-derivative of V with sodium methoxide. This *tricyclo*nonanedionetetracarboxylic ester takes up two molecules of methyl alcohol when it is treated with methyl alcoholic sodium methoxide. The last-formed bridge remains intact and the product is a methyl *cyclo*heptanehexacarboxylate for which there are three possible formulæ. Numerous further derivatives of these interesting substances have been prepared. It should be pointed out that the configuration of the *cyclo*heptane ring obtained by opening up the *tricyclo*nonane system is one which has screw asymmetry independent of the substituents.

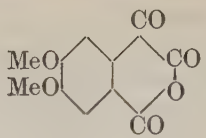
Tautomerism.

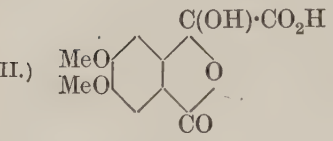
An addition to the literature which will be generally welcomed is the "Report on Some New Aspects of Tautomerism," by J. F. Thorpe and C. K. Ingold, published under the auspices of the *Union Internationale de la Chimie Pure et Appliquée*. The brochure is an admirable summary of the more important developments in the work of the School which has so successfully attacked some of the most difficult theoretical problems of Organic Chemistry.

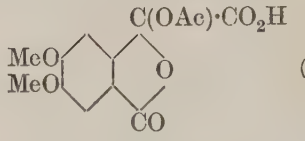
Ring-chain Tautomerism.—Although not strictly speaking a case of tautomerism, the properties of 4 : 5-dimethoxyphthalonic acid have an interest of a related character.[74] The substance crystallises from water with $2H_2O$, and one of the molecules of water is lost at 100°. The anhydrous acid crystallises from an ethereal solution dried over sodium sulphate. What is remarkable is the differing behaviour of these specimens towards acetyl chloride. The hydrated acid (I) is converted into the yellow anhydride (II), whereas the anhydrous acid (III), which is called dimethoxy-ψ-phthalonic acid, is transformed into an acetyl derivative (IV).

[74] W. H. Perkin and (Miss) C. Kuroda *T.*, 1923, 123, 2094.









The products of the action of alkalis on αα′-dibromo-ββ′-dialkylglutaric esters have been examined in many new cases, the main object in view being the determination of the effect of varying the substituents R, R′ on the equilibrium

$$RR'C\begin{<}CO\cdot CO_2H\\CH_2\cdot CO_2H\end{>} \rightleftharpoons RR'C\begin{<}C(OH)\cdot CO_2H\\CH\cdot CO_2H\end{>}$$

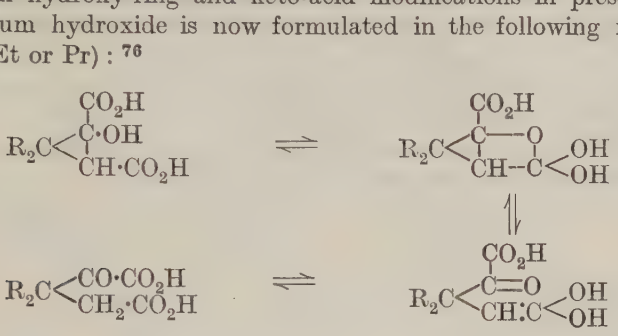
It will be recalled that when the groups RR′ are both hydrogen or methyl, the keto-acid alone can be obtained, whilst if RR′ is pentamethylene the hydroxy-ring acid constitutes the whole product; further, that an equilibrium is set up in presence of concentrated potassium hydroxide solution when R and R′ are ethyl groups. It has now been found that RR′ = MeEt [75] and RR′ = tetramethylene [76] present cases similar to that where R and R′ are methyl groups, but that when R and R′ are propyl groups there is again an equilibrium in presence of potassium hydroxide.[77] This is more in favour of the hydroxy-ring acid than was found to be the case in the diethyl series. These results strongly support the hypothesis of the gonal relations of the carbon valencies. Widening of the angle in one pair of valencies narrows it in the other, and it is, of course, the reduced natural angle of the valencies which brings the carbonyl group in these ketoglutaric acids into closer proximity with the methylene group in the β-position, and so favours the formation of a *cyclo*propane ring by aldol condensation. In those examples where the keto-acid is definitely favoured, the action of alcoholic potassium hydroxide produces alkyloxy*cyclo*propane derivatives, as shown in the scheme:

$$MeEtC\begin{<}CHBr\cdot CO_2Et\\CHBr\cdot CO_2Et\end{>} \xrightarrow{\text{alcoholic KOH}} MeEtC\begin{<}C(OEt)\cdot CO_2K\\CH\cdot CO_2K\end{>}$$

The instability of the hydroxy-ring acids is, however, demon-

[75] B. Singh and J. F. Thorpe, *T.*, 1923, **123**, 113.
[76] E. W. Lanfear and J. F. Thorpe, *ibid.*, p. 1683.
[77] L. Bains and J. F. Thorpe, *ibid.*, p. 1206.

strated by the fact that these alkyloxy-derivatives are converted by acid hydrolysis into the open-chain keto-acids. The interchange between hydroxy-ring and keto-acid modifications in presence of potassium hydroxide is now formulated in the following manner (R = Et or Pr) : [76]



This hypothesis, which implies that a case of ring-chain tautomerism is fundamentally intra-annular, is entertained on account of the fact that there is evidence available which shows that the *trans*- and not the *cis*-forms of the hydroxy-ring acids undergo fission.

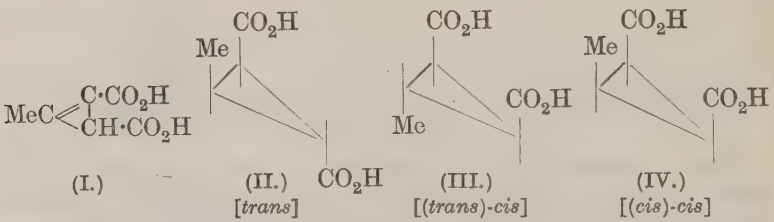
The view formerly tentatively expressed that Balbiano's acid, $CO_2H{\cdot}CHMe{\cdot}CMe_2{\cdot}CO{\cdot}CO_2H$, exhibits twofold ring-chain tautomerism has now been modified, because there is no sufficient evidence of the existence of a hydroxy-ring (*cyclo*propane) phase.[78] The argument is too complex to be usefully summarised, but the conclusion drawn is that the behaviour of this and related trialkylated acids is to be expressed by the scheme :

Three-carbon Systems.—A detailed investigation of 3-methyl-*cyclo*propene-1 : 2-dicarboxylic acid and its derivatives [79] has furnished results of considerable theoretical importance which it is probably not too much to say establish firmly the correctness in broad outlines of the conception of the glutaconic acid system which is due to J. F. Thorpe. In the open-chain glutaconic acids the possibility of *cis-trans*-isomerism always presented a loophole, but the characteristic features of the system have now been found to be reproduced in the case of a substance which, on the ordinary theory, cannot exist in *cis*- and *trans*-forms. The preparation of the *cyclo*propene acid by known methods has been so much improved

[78] K. C. Pandya and J. F. Thorpe, *T.*, 1923, **123**, 2852.
[79] F. R. Goss, C. K. Ingold, and J. F. Thorpe, *ibid.*, pp. 327, 3342.

that 1 kilogram may be obtained from 6 kilograms of ethyl aceto-acetate. If a conventional symbol is to be assigned to it, the expression (I) must be chosen for the following reasons *inter alia* :—

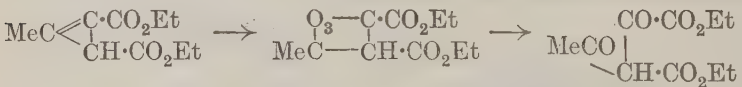
(i) The formula is in harmony with all known methods of formation, for example, from bromo*iso*dehydracetic ester and from $\alpha\alpha'$-dibromo-β-methylglutaric ester under the influence of alkali. Still more interesting is the synthesis of the acid by the removal of two hydrogen atoms from each of the three stereoisomeric methyl-*cyclo*propanedicarboxylic acids (II, III, IV).



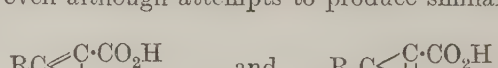
(ii) The *cyclo*propene acid is not affected by mild reducing agents, but yields β-methylglutaconic acid when heated with hydriodic acid with or without the addition of phosphorus.

(iii) The additive properties of the substance characterise it as an αβ-unsaturated acid.

(iv) The acid is oxidised by alkaline permanganate to malonic acid, and its esters yield an ozonide which furnishes ethyl acetyl-oxaloacetate (V) on reduction.*



The statement of Feist [80] that the acid exists in two forms, m. p. 200° and m. p. 189°, has been challenged, since the latter is shown to be an impure specimen of the former. We should probably, on this and other evidence, be quite satisfied with the formula I for the acid, even although attempts to produce similar substances of the types

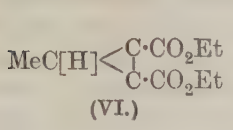


have invariably been fruitless, were it not for the fact that the behaviour of the esters can only be explained by the adoption of a special structural theory which has a repercussion on our view of

* In this reaction the "normal" ester exhibits the more unsaturated character and the fact that it absorbs ozone more rapidly than the labile ester is of very great importance. It is this observation which renders the hypothesis that the acid and its "normal" ester are Δ^1-derivatives untenable.

[80] *Ber.*, 1893, **26**, 750.

the acid itself. Esterification by means of the usual agents gives a mixture of three esters—the "normal," the "labile," and the "enol" esters—to which the symbol VI and the constitutions VII and VIII have been respectively assigned.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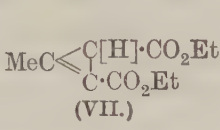
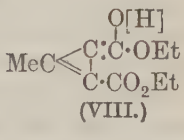

(VII.)


(VIII.)

These esters have been proved to be in equilibrium with one another, and in a hot alcoholic solution containing a mineral acid the following mixture is obtained:

$$\underset{(95\%)}{\text{Normal ester}} \rightleftharpoons \underset{(5\%)}{\text{Labile ester}} \rightleftharpoons \underset{(\text{trace})}{\text{Enol ester}}$$

In sodium ethoxide solution at 60°, the equilibrium is stated to be represented by the scheme (ethyl esters):

$$\underset{(40\%)}{\text{Normal ester}} \rightleftharpoons \underset{(\text{trace})}{\text{Labile ester}} \rightleftharpoons \underset{(\text{trace})}{\text{Enol ester}} \rightleftharpoons \underset{(60\%)}{\text{Sodio-derivative}}$$

The "normal" ester, m. p. 38—39°, possesses the closest relation to the free acid, being the sole product of the action of ethyl iodide on the silver salt. It is the form into which the others tend to be predominatingly transformed, and is characterised by its stability towards additive reagents (except ozone) and by its inability to yield a sodio-derivative without previous conversion into the "labile" isomeride. The "normal" and "labile" esters can be separated by fractional distillation in a vacuum, but when the "normal" ester is distilled under the ordinary pressure, the pure "labile" ester condenses in the receiver. The "labile" ester is distinguished from the "normal" ester by the fact that it rapidly yields a yellow sodio-derivative (of the enol ester) when treated with cold dilute alcoholic sodium ethoxide. The enol ester is distinguished from its isomerides by its yellow colour, its solubility in cold dilute sodium hydroxide, and by the immediate and intense coloration which it gives with ferric chloride.

The series is seen to be precisely analogous to the "normal," "labile," and "enol" forms of glutaconic acids or their derivatives in the aliphatic series. Since *cis-trans*-isomerism is here precluded, the existence of the "normal" forms may be regarded as established. These "normal" glutaconic acid derivatives have two of the chief characteristics of benzenoid or aromatic systems. In the first place, they are readily formed, often by unusual reactions, and show a great tendency to preserve their type, and in the second place there is a decided reduction of the unsaturated

character evinced by the double bond. It might be added that they often exhibit considerable crystallising power. For these reasons the "normal" forms have also been described as semi-aromatic. The elucidation of the nature of these substances is accordingly a matter of importance in connexion with the theory of aromatic types. It is not, perhaps, surprising that little progress has been made in this direction—the first thing was to provide convincing proof of the existence of the normal forms. Nevertheless the following remarks of the authors of the paper under discussion may be quoted as an indication of the type of hypothesis which they tend to adopt:—"In the 'normal' formula, as in all formulæ of the normal glutaconic type, the mobile hydrogen atom is placed at the centre of the three-carbon (glutaconic) system, in order to indicate that this three-carbon system represents the extent of what may loosely be described as the orbit of the hydrogen atom. Thus the 'normal' formula is essentially a dynamic formula. . . ." It is difficult to grasp exactly what this theory implies, unless it is a return in a particular case to the oscillation hypothesis of Laar. The reporter is not aware of any experimental evidence which is better interpreted on such a view than on that which ascribed the stability of the normal forms to a relatively static molecule and a co-ordinated hydrogen atom. Is not the fact that the "labile" ester is produced by heating the "normal" ester an indication that the internal molecular energy of the former is the greater?

*cyclo*Propene itself, $CH_2<\begin{matrix}CH\\ \|\\ CH\end{matrix}$, has been obtained by the thermal decomposition of *cyclo*propyltrimethylammonium hydroxide.[81] The gas may be condensed to a liquid by means of ether and solid carbon dioxide. It is extremely unsaturated, polymerising in light and absorbing oxygen. It unites very energetically with bromine and forms an iodide when treated with an alcoholic solution of iodine.

It is natural that search should be made for examples of three-carbon tautomerism outside the glutaconic acid series and an example has been found in *cyclo*hexenylacetone (IX), which is thought to be tautomeric with *cyclo*hexylideneacetone (X).

$CH_2<\begin{matrix}CH_2—CH_2\\ CH_2—CH\end{matrix}>C\cdot CH_2\cdot COMe$ (IX.) $CH_2<\begin{matrix}CH_2—CH_2\\ CH_2—CH_2\end{matrix}>C{:}CH\cdot COMe$ (X.)

(XI.) $CH_2<\begin{matrix}CH_2—CH_2\\ CH_2—CH\end{matrix}>C\cdot CHEt\cdot COMe \rightleftharpoons \begin{matrix}-CH_2\\ -CH_2\end{matrix}>C{:}CEt\cdot COMe$

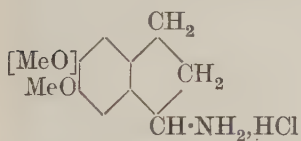
[81] N. J. Denjanov and M. Dojarenko, *Ber.*, 1923, **56**, [*B*], 2200; *A.*, i, 1188.

Reactions corresponding to both forms were already known, and it has now been found that the distinct chlorides of pure Δ^1-*cyclo*hexeneacetic and *cyclo*hexylideneacetic acids give one and the same ketone when condensed with zinc methyl iodide.[82]

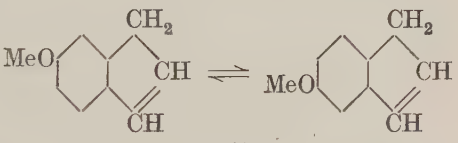
Furthermore, the ketone gives a weak coloration with ferric chloride in alcoholic solution, and with alcoholic sodium ethoxide gives an orange-yellow solution of a sodio-derivative, which is transformed by ethyl iodide into the ethyl derivative (XI). This substance was synthesised by an independent method.

The tautomerism which is proved by these experiments does not appear to be that which involves the individuals IX and X, but is rather between X and the enol form of IX, which is, in its turn, in equilibrium with IX. It is therefore in all probability a case of tautomerism analogous to that of anthrone, that is, keto-enol tautomerism where the methylene and carbonyl groups are separated by a double bond or an equivalent system.

The tautomeric character of the indene nucleus has long been suspected, but experiments now placed on record offer a proof that the system is mobile to at least the same extent as a typical benziminazole.[83] 5- and 6-Methoxyhydrindamine hydrochlorides (XII) yield, on heating, one and the same methoxyindene (XIII) and ammonium chloride.



(XII.)



(XIII.)

This is called the "symmetry" test for mobility. The methoxyindene yields isomeric benzylidene derivatives and thus satisfies the "substitution" test. Only the "fission" test failed to provide evidence of tautomerism, because the only significant oxidation product isolated was the methoxyhomophthalic acid derived from the first figured component of the equilibrated mixture (XIII). Obviously indene may have a constitution analogous to that of a normal glutaconic acid. A remarkable observation was made in the course of the work. *p*-Nitro-β-phenylpropaldehyde, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CHO$, was obtained by the action of aluminium chloride on *p*-nitro-β-phenylpropionyl chloride in thionyl chloride solution. The yield was only 15 per cent. of that theoretically possible, but 75 per cent. of the chloride used was recovered in the form of the corresponding acid.

[82] S. F. Birch, G. A. R. Kon, and W. S. G. P. Norris, *T.*, 1923, **123**, 1361.
[83] C. K. Ingold and H. A. Piggott, *ibid.*, p. 1469.

The Theory of Aromatic Types.

Opinion is crystallising in connexion with the problem of the constitution of benzene, but unfortunately it is also exhibiting the property of polymorphism. Those who regard the question from the point of view of an attempt to employ the electronic theory of valency as a generalisation in organic chemistry appear more and more to converge on the idea that there are groups of electrons which by their association confer a new factor of stability on the molecule. If we take it that systems possessing aromatic character are such as exhibit reduced unsaturation of the component parts coupled with a tendency to formation and to preservation of type, then molecular nitrogen, compounds containing the carboxyl group, glutaconic acids, *cyclo*pentadienes, thiophen, and benzene can all be regarded as aromatic and also as containing groups of two, four, or six electrons which have a special function. This theory is on safe ground so long as it is not too ambitiously employed. Attempts to deduce space models on an electronic basis are, however, almost useless unless such models accommodate all the known facts, including the molecular symmetry of fused or dissolved benzene derivatives and the reduced symmetry of the crystal molecules.[84] We conclude that the time has not yet arrived when the electronic theory of benzene can be stated in precise terms and this is not surprising when it is considered that the physical meaning of the simple non-polar linking has not yet been satisfactorily explained. Indeed, the whole electronic theory of valency must be employed at the present time in a symbolic fashion. Quite a different point of view is that of those chemists who, employing the conventional valency symbols, regard the aromatic compounds as tautomeric systems comprising different individuals to which precise constitutional formulæ can be assigned.[85] The reporter does not share the conviction that a complete solution of the benzene problem is possible along these lines, but the classical theory combined with the hypothesis of intra-annular tautomerism has been made the basis of much valuable experimental work, a prominent position among which is occupied by an extremely interesting comparison of the properties of the *cyclo*pentadiene and benzene nuclei.[86] Previous work [87] had led

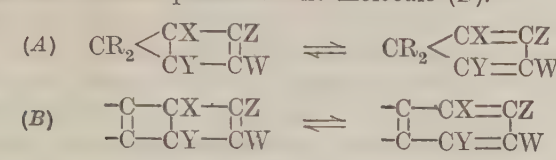
[84] Compare B. Orelkin, *J. Russ. Phys. Chem. Soc.*, 1923, **54**, 493; *A.*, i, 1082.

[85] Compare W. A. P. Challenor and C. K. Ingold, *T.*, 1923, **123**, 2066; C. K. Ingold, *ibid.*, p. 2081.

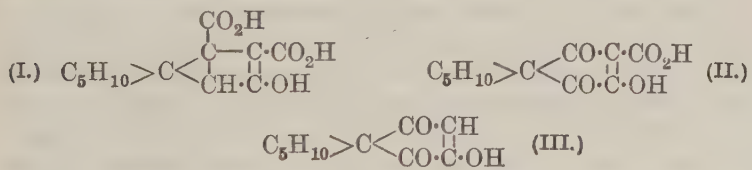
[86] C. K. Ingold, E. A. Seeley, and J. F. Thorpe, *ibid.*, p. 853.

[87] E H. Farmer and C. K. Ingold, *T.*, 1920, **117**, 1362; E. H. Farmer, C. K. Ingold, and J. F. Thorpe, *T.*, 1922, **121**, 128; *Ann. Reports*, 1922, **19**, 112.

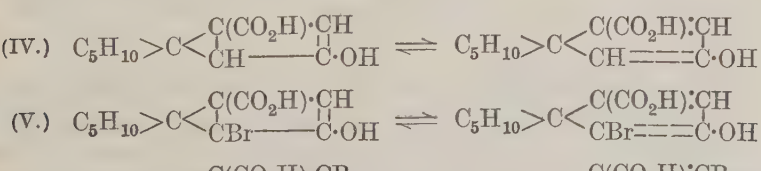
to the conclusion that there exists in certain five-carbon nuclei a tautomeric condition characterised by exchanges (*A*) which may be compared with those postulated in the benzene series between Dewar and Kekulé phases of the molecule (*B*).



When the group CR_2 is CMe_2, in a certain series of the above kind, the experimental verification of the analogy with benzene is difficult on account of the stability of the bridge-bond. If, however, the group is *cyclo*hexylidene, theory indicates a weakening of the bridge, and this conclusion has been justified by experiment.[88] These *cyclo*hexane*spirocyclo*pentadiene derivatives were therefore selected as a group of compounds which should simulate those properties of benzene derivatives which can be laid to the account of the severance of a para-linking. It was, indeed, found in numerous cases that the normal mode of oxidation led to the production of diketones, the *p*-quinones of the five-carbon nucleus. One example may be cited. The hydroxy-acid (I) is quantitatively converted by an alkaline solution of potassium ferricyanide into the quinonoid compounds (II and III).



The action of halogens on the *cyclo*pentadienes is shown in suitable cases to involve two kinds of aromatic simulation, that is, (i) formation of substitution products or preservation of type, and (ii) the formation of blocked perhalogenated derivatives. These points may be briefly illustrated by a consideration of the course of the bromination of the acid IV.



[88] C. K. Ingold and J. F. Thorpe, *T.*, 1919, **115**, 120.

The first bromine atom enters the position shown in V and the second in the remaining ortho-position to the hydroxyl group. In the case of both the bromo- and the dibromo- (VI) acid, oxidation products were obtained indicating the predominance of the bridged phases, but including also some derivatives of aconitic acid, which may be regarded as obtained from the double-bonded phases. VI is converted by further bromination into the blocked tribromo-acid (VII), which on oxidation is converted into a bromohydroxy-semi-quinone (VIII). The reaction doubtless takes place through the intermediate figured below, this substance being spontaneously reduced by alkali by a reaction analogous to that characteristic of other cyclic compounds containing the group $-CO-CBr_2-CO-$.

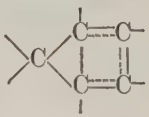
(VII.) $C_5H_{10}>C<\begin{matrix}C(CO_2H)\cdot CBr_2\\ CBr-\!\!-CO\end{matrix} \rightarrow C_5H_{10}>C<\begin{matrix}CO\cdot CBr_2\\ CO\cdot CO\end{matrix} \rightarrow$

$C_5H_{10}>C<\begin{matrix}CO\cdot CBr\\ CO\cdot C\cdot OH\end{matrix}$ (VIII.)

A very noteworthy transformation is the conversion of the bromo-enolic acid (V) into the dienol (IX), which is effected by boiling alkali:

(IX.) $C_5H_{10}>C<\begin{matrix}C(OH)\cdot CH\\ CH-\!\!-C\cdot OH\end{matrix} \rightleftharpoons C_5H_{10}>C<\begin{matrix}C(OH):CH\\ CH=\!=C\cdot OH\end{matrix}$

Compounds of this type exhibit analogies with resorcinol and the formation of 1 : 3-dihydroxy-compounds from a 1 : 2-bromo-hydroxy-derivative is compared with the production of resorcinol from *o*-bromophenol by the action of alkali at high temperatures. The reaction in both cases is attributed to the hydrolytic fission of a bridge-bond, but it should be noted that the bridge assumed in *o*-bromophenol is not the one which a consideration of its properties as a phenol would require on this hypothesis. The interpretation given above is that of the authors, but in view of the importance of the subject it may not be out of place to suggest that the experimental data may also be explained on the basis of the formula

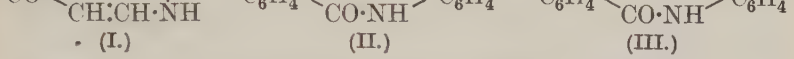


for the *cyclo*pentadiene nucleus. In the course of reactions, the four electrons represented by the dotted lines can regroup themselves in such a way as to increase or decrease the value of the bridge partial valency. The final solution of this constitutional problem is probably beyond the reach of the ordinary methods of organic chemistry and must await some definite advance in

technique, possibly in connexion with the analysis of crystals. It is not too optimistic to look forward with confidence to the time when the electronic distribution in the molecules of carbon compounds will be disclosed by physical methods.

Molecular Rearrangement.

Some examples of the enlargement of the rings of quinones by the Beckmann transformation have been recorded.[89] *p*-Benzoquinonemonoxime yields a benzenesulphonyl ester which breaks down on heating and subsequent treatment with sulphuric acid so as to form the substance I, which has pronounced acidic properties.

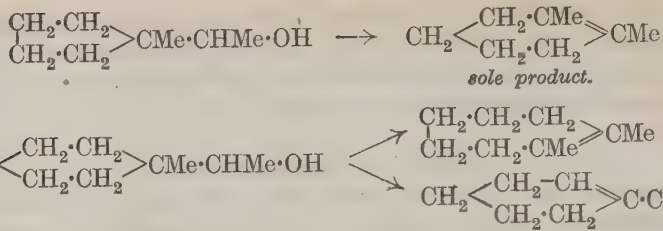


(I.) (II.) (III.)

Anthraquinonemonoxime is converted by a mixture of phosphorus pentachloride and acetyl chloride into the cyclic amide (II), which yields an oxime capable of transformation into phthal-*o*-phenylenediamide (III). Numerous investigations of the course of pinacol–pinacolin and semi-pinacolic transformations have been published during the year and some generalisations have emerged. It is, for example, definitely shown that ethyl and benzyl groups have a much greater migrational aptitude than the methyl group.[90]

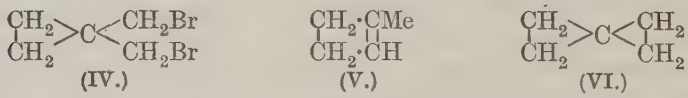
In the case of alkylhydrobenzoins, OH·CHPh·CRPh·OH, the action of sulphuric acid may lead either to a phenyl α-alkylbenzyl ketone, COPh·CHRPh, by dehydration ("tertiary"-OH reactive) or to a benzhydryl alkyl ketone, $CHPh_2$·COR, by migration ("secondary"-OH reactive). When R is a group of strong "saturation" capacity, for example, methyl, *iso*butyl, or phenyl, the former type of reaction occurs. On the other hand, when R = ethyl, *n*-butyl, propyl, *iso*amyl, both types of reaction occur. The influence of the nature of the group R may make the secondary hydroxyl more reactive than the tertiary.[91] The relative freedom of the *cyclo*heptane ring from strain, to which reference is made above, is regarded as the explanation of the formation of seven-rings in the Wagner-type rearrangement of certain *cyclo*hexane derivatives. The following comparison nevertheless proves that there is more resistance to overcome in passing from six- to seven-ring members than is the case in the enlargement from five to six.[92]

[89] E. Beckmann and O. Liesche, *Ber.*, 1923, **56**, [*B*], 1; *A.*, i, 232.
[90] M. Tiffeneau and (Mlle) J. Levy, *Compt. rend.*, 1923, **176**, 312; *A.*, i, 213.
[91] M. Tiffeneau and A. Orékhoff, *ibid.*, 1922, **175**, 964; *A.*, i, 113.
[92] H. Meerwein and J. Schäfer, *J. pr. Chem.*, 1922, [ii], **104**, 289; *A.*, i, 324.

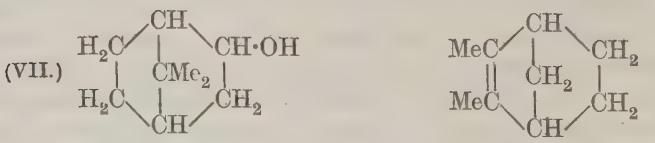


This may, however, have something to do with the fact that it is much easier to introduce a double bond into the *cyclo*hexane than into the *cyclo*pentane ring. Thus *cyclo*pentane is passive towards fuming sulphuric acid under conditions whereby hydroaromatic hydrocarbons are readily oxidised.[93] On the other hand, 1 : 1-dimethyl*cyclo*hexane, which is not hydroaromatic, resists dehydrogenation to a much greater extent than *cyclo*hexane. It is not affected by passage over very active platinised asbestos at 300°.[94]

The reduction of ωω-dibromo-1 : 1-dimethyl*cyclo*propane (IV) with zinc dust and alcohol leads to a hydrocarbon, C_5H_8,[95] which has now been found to yield lævulic and succinic acids on oxidation and therefore is methyl-Δ^1-*cyclo*butene (V) or, much less probably, methylene*cyclo*butane.[96] This shows that the process cannot proceed by way of the *spiro*-compound (VI) and provides an additional argument against the validity of the tricyclene explanation of the Wagner-Meerwein transformation of borneol.



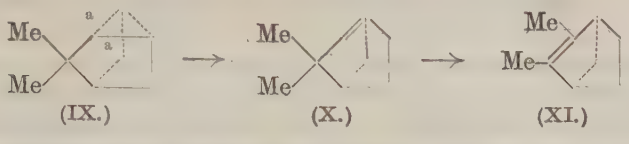
The tricyclene hypothesis is, however, very frequently employed, and has been advanced in order to explain the complex rearrangement which fenchocamphorol (VII) suffers when it is heated with potassium hydrogen sulphate. The product is santene (VIII).



α- and β-Fenchocamphorol and camphenilol can yield the same

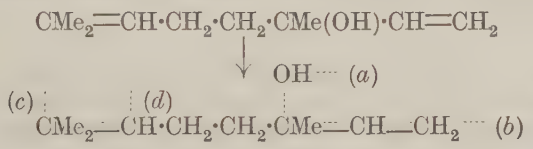
[93] N. Zelinski, *Ber.*, 1923, **56**, [*B*], 1718; *A.*, i, 907.
[94] N. Zelinski and (Frl.) N. Delzova, *ibid.*, p. 1716; *A.*, i, 907.
[95] N. Zelinski, *Ber.*, 1913, **46**, 160.
[96] C. K. Ingold, *T.*, 1923, **123**, 1706.

tricyclene (IX), which by rupture of one of the bonds (a) yields the unstable intermediate (X) and then santene (XI).[97]

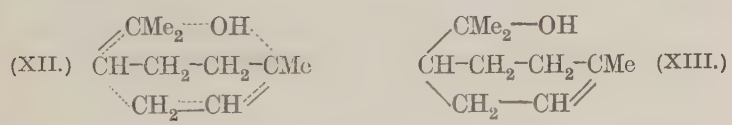


(IX.) (X.) (XI.)

The rearrangement of fenchocamphorol to santene can, however, be readily represented on the reporter's cyclic partial valency theory,[98] the ring involving eight members. It has been urged as an objection to the tricyclene hypothesis that, since tricyclene is symmetrical, it cannot give rise to an optically active product. Ruzicka and Liebl consider that this objection cannot be maintained, because in the case of the transformation of active linalool into active terpineol, the asymmetric centre is changed from one carbon atom to another, and on any hypothesis there must be an intermediate stage which is symmetrical. One is grateful for such an excellent illustration of the advantages of the cyclic partial valency theory of migration. In accordance with this view the change in question is to be represented in the following manner :



If (*a*) and (*b*) unite, the result would be to produce geraniol. Terpineol results from the addition of (*a*) to (*c*) and (*b*) to (*d*), giving the stage XII.



(XII.) (XIII.)

This, by further rearrangement in the same sense, yields terpineol (XIII), the whole process being continuous.

Owing to the fact that the intermediate is a "caged" ring (cineole-type) the terpineol formed not only can, but must, be optically active unless, of course, racemisation occurs before or after the transformation. It cannot occur during the change.

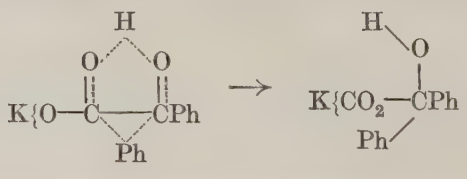
Several papers deal with the mechanism of the conversion of benzil into benzilic acid under the influence of alkalis. This reaction is regarded from two points of view, that is, as an internal

[97] L. Ruzicka and Fr. Liebl, *Helv. Chim. Acta*, 1923, **6**, 267; *A.*, i, 475.
[98] *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 4.

oxidation–reduction presenting points of analogy with the addition of an organo-metallic compound to a ketone or alternatively as a pinacol–pinacolin-type rearrangement preceded by addition of the reagent to both carbonyl groups. The former theory is to some extent supported by the discovery that a definite compound, $C_{14}H_{10}O_2$,KOH, can be isolated by trituration of the components under pyridine or benzene. This substance is decomposed by water with regeneration of benzil and potassium hydroxide. It is slowly converted at 0°, in a few hours at the ordinary temperature, and very rapidly at 80° into potassium benzilate, so that it appears to be a true intermediate product in the transformation.[99] A similar compound of potassium methoxide and benzil is stable, whilst another investigator finds that the additive product of sodium ethoxide and benzil breaks down in cold alcoholic solution with formation of benzaldehyde and ethyl benzoate.[1] The fact that only one molecule of the reagent is requisite in order to transform one molecule of the diketone emerges as the result of still another research.[2]

These facts are embraced by the hypothesis that the reaction is a rearrangement of the negative ion of the additive compound, PhC(OH)·COPh
O}K

The charged =C(OH)–O– group strives to stabilise itself by becoming a true ion of a carboxylic acid. To do this, it loosens both a hydrogen atom and a phenyl group, which add on to the neighbouring carbonyl. An intermediate stage can be represented on the partial valency theory by the expression



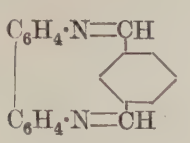
The Cannizzaro reaction can be explained in a precisely similar manner. The additive product Ph–CH(OH)–O}K gives up two hydrogen atoms in order to accommodate the negative charge in the benzoic anion.

Stereochemistry of Diphenyl Derivatives.

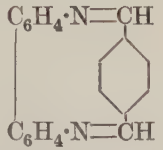
Benzidine and some of its derivatives condense with *iso*phthalaldehyde and terephthalaldehyde to form coloured, extremely

[99] G. Scheuing, *Ber.*, 1923, **56**, [*B*], 252; *A.*, i, 231.
[1] A. Lachman, *J. Amer. Chem. Soc.*, 1923, **45**, 1509; *A.*, i, 784.
[2] A. Schönberg and K. T. Keller, *Ber.*, 1923, **56**, [*B*], 1638; A., i, 928.

sparingly soluble substances which may have the following structures :



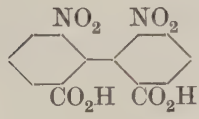
and

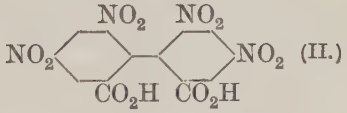


These compounds may, however, be polymerides.[3] Some further details in connexion with the isomeric *oo*-dinitrobenzidines have been recorded.[4] An independent synthesis of the isomeride obtained by hydrolysis of the product of nitration of diacetylbenzidine has confirmed the view that this substance is 3 : 5′-dinitrobenzidine. Furthermore, the tetra-amino-compounds obtained by reduction of 3 : 3′- and 3 : 5′-dinitrobenzidines have been found to be different substances, although they yield the same diquinoxaline on condensation with benzil. The observation that γ-6 : 6′-dinitrodiphenic acid (I) can be resolved into optically active components has been followed up, and further examples of enantiomorphous diphenyl derivatives have been found.

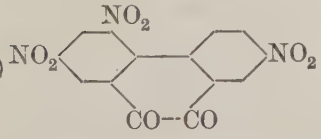
The isomeric 6 : 6′-dinitrodiphenic acids yield on nitration only one 4 : 6 : 4′ : 6′-tetranitrodiphenic acid (II), which is regarded as the γ-variety because it may be resolved.[5] An attempt was then made to produce a stereoisomeride of this acid by oxidation of 2 : 4 : 5 : 7-tetranitrophenanthraquinone. The latter substance, however, could not be obtained by nitration of 2 : 7-dinitrophenanthraquinone, since, for some reason, one nucleus resists nitration.

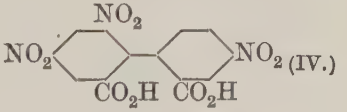
The product was 2 : 4 : 7-trinitrophenanthraquinone (III) and this yields, on oxidation, 4 : 6 : 4′-trinitrodiphenic acid (IV), which was resolved into optically active modifications.[6]

(I.)




(II.)

(III.)




(IV.)

[3] R. Adams, J. E. Bullock, and W. C. Wilson, *J. Amer. Chem. Soc.*, 1923, **45**, 521; *A.*, i, 378.

[4] O. L. Brady and G. P. McHugh, *T.*, 1923, **123**, 2047.

[5] G. H. Christie and J. Kenner; *T.*, 1922, **121**, 614.

[6] *Idem.*, *T.*, 1923, **123**, 779.

This shows that one nitro-group in the *o*-position to the coupling link suffices to ensure stability of the asymmetric configuration of the diphenic acids. Furthermore, the resolution of 6 : 6′-dichlorodiphenic acid has been successfully accomplished and therefore nitroxyl groups are not to be regarded as necessary components of resolvable diphenic acids.[7] It is very curious that an anhydride cannot be obtained from 4 : 4′-dinitrodiphenic acid [8] or diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid. This discounts the value of the argument against the Kaufler diphenyl configuration, which might be advanced as the result of the observation that diphenyl-3 : 5 : 3′ : 5′-tetracarboxylic acid cannot be dehydrated.[9]

Triphenylmethane Derivatives.

Triphenylmethyl chloride reacts with alcohols in the presence of anhydrous pyridine with formation of ethers, $CPh_3 \cdot OR$. These ethers crystallise well, and may possibly be employed for the characterisation or even the purification of alcohols.[10] They are quite stable to boiling alcoholic alkali, but are hydrolysed by dilute methyl-alcoholic hydrogen chloride in the cold. The products are the alcohol R·OH and triphenylcarbinyl methyl ether. The reactivity of groups attached to the triphenylmethyl residue is exemplified in a series of double decompositions.[11] Triphenylmethylcarbinol gives moderate yields of triphenylmethylamine, $CPh_3 \cdot NH_2$, and triphenylmethylaniline, $CPh_3 \cdot NHPh$, when treated in boiling acetic acid solution with ammonium or aniline acetate, respectively. Triphenylmethylaniline is converted by heating in a sealed tube with alcoholic ammonia into triphenylmethylamine under conditions which leave triphenylcarbinol unaffected. Similarly, triphenylmethylamine yields triphenylmethylaniline by the action of an excess of aniline. *o*-Hydroxytriphenylcarbinol exhibits a reversible colour change in solution at temperatures between 50° and 110°. This is supposed to be due to the formation of a quinonoid form and the hypothesis is supported by the fact that above 100° the expected *o*-fuchsone (I) rearranges to 9-phenylxanthane (II).

[7] G. H. Christie, C. W. James, and J. Kenner, *T.*, 1923, **123**, 1948.

[8] J. Schmidt, *Ber.*, 1903, **36**, 3743.

[9] H. Burton and J. Kenner, *T.*, 1923, **123**, 1043.

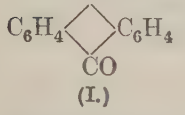
[10] B. Helferich, P. E. Speidel, and W. Toeldte, *Ber.*, 1923, **56**, [*B*], 766; *A.*, i, 331.

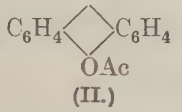
[11] P. I. Petrenko-Kritschenko and A. Gandelman, *J. Russ. Phys. Chem. Soc.*, 1917, **49**, 413; *A.*, i, 554.

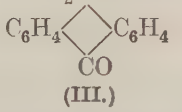
This is a type of quinonoid addition familiar in connexion with the chemistry of the azine-dyestuffs. *o*-Hydroxytriphenylmethyl could only be isolated in the form of a polymeride.[12]

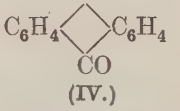
The Anthracene Group.

To the already strong evidence that in substitution reactions it is the enolic modification of a phenol which is reactive must now be added the outcome of a striking experiment with phenylanthrone (I). This substance is non-fluorescent in acetic acid solution, and therefore does not contain an anthracene nucleus. It should be mentioned that derivatives of the enol form, for example, the methyl ether, exhibit powerful fluorescence in solution. Phenylanthrone was found to be unattacked by nitric acid in acetic acid suspension under conditions more vigorous than those which suffice to transform phenylanthranyl acetate (II) into a mixture of phenylnitroanthrone (III) and phenylhydroxyanthrone (IV). Phenylnitroanthrone alone is formed in the facile nitration of phenylanthranyl methyl ether in acetic acid solution.[13]


(I.)


(II.)


(III.)

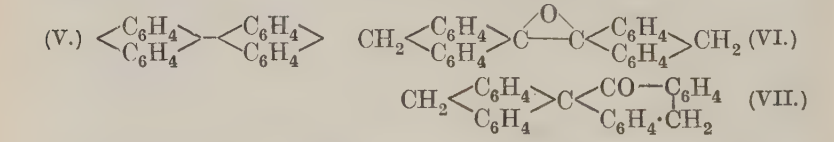

(IV.)

Phenylanthrone is conveniently prepared by the condensation of bromoanthrone and benzene in the presence of aluminium chloride, and on reduction with zinc dust and ammonia it is very readily changed to phenylanthracene. The above reactions are attributed to 9 : 10-addition involving the rupture of the "bridge bond" which is supposed to connect these atoms. The important point is the 9 : 10-addition, not the theory of the mechanism of it, the sole recommendation of which is its convenience. The relations of anthracene with anthraquinone are exhibited clearly enough by means of a "bridge" bond, but this is scarcely true of pyrene and pyrenequinone, of dianthranol and dianthraquinone, and in general of heteronuclear quinols and quinones. It is now suggested that "bridge" bonds, being unsaturated, may be conjugated. If, however, conjugation as an explanation of additive phenomena is to be admitted at all, in what respects, it may be asked, does the "bridge," essentially a device for avoiding conjugation, offer any advantages? When anthrone is reduced by means of zinc and hydrochloric acid, it yields a mixture of dianthranyl (V) and

[12] M. Gomberg and D. Nishida, *J. Amer. Chem. Soc.*, 1923, **45**, 190; *A.*, i, 212.
[13] E. de B. Barnett and J. W. Cook, *T.*, 1923, **123**, 2631.

an α-pinacolin to which the ethylene-oxide structure (VI) has been assigned.

The intermediate pinacol derived from anthrone loses water in two directions. When the substance VI is heated in acetic acid solution with hydrochloric acid, it probably adds on water with reproduction of the pinacol, which is immediately dehydrated with formation of dianthranyl. This behaviour coupled with the refusal of the substance to form an acetate or benzoate is regarded as proving the ethylene-oxide structure.[14] It is, however, quite conceivable that the substance is a real keto-pinacolin with a seven-ring (VII), because it seems very probable that the pinacol–pinacolin transformation is reversible, although the equilibrium may greatly favour the pinacolin. In such a case as the present one, the irreversible conversion of the pinacol into an aromatic substance would ensure the transformation of the whole of the product, however small the proportion of pinacol in the equilibrated mixture.



The fact that the arylamine salts of the anthraquinone mono- and di-sulphonic acids exhibit a great tendency to crystallise and are sparingly soluble in water and alcohol is of much practical interest.

For example, pure methylaniline can be separated from a mixture containing not too much dimethylaniline by taking advantage of the sparing solubility of methylaniline anthraquinone-2-sulphonate.[15] The dry distillation of sodium anthraquinone-2-sulphonate was examined in 1885,[16] but the nature of the products has only recently been elucidated.[17] The chief substances formed are 2 : 2′-dianthraquinonyl ether and the corresponding sulphide, which is an orange-red substance.

Michler's ketone and anthrone condense together slowly in boiling benzene solution in presence of phosphoryl chloride with formation of a product from which 4′ : 4″-tetramethyldiamino-anthrafuchsone (VIII) can be isolated in 62 per cent. yield.[18] This is a brick-red substance which gives bright blue salts of the usual

[14] E. de B. Barnett and M. A. Matthews, *T.*, 1923, **123**, 380.

[15] A. G. Perkin and W. G. Sewell, *J. Soc. Chem. Ind.*, 1923, **42**, 27T; *A.*, i, 234.

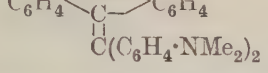
[16] A. G. Perkin and W. H. Perkin, *T.*, 1885, **47**, 679.

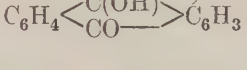
[17] A. G. Perkin and W. G. Sewell, *T.*, 1923, **123**, 3032.

[18] F. A. Mason, *ibid.*, p. 1546.

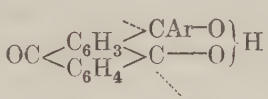
quinonoid triphenylmethane type. The colour-salt is readily hydrolysed by water, but with formation of a substance of much darker colour than the fuchsone, and this is thought to be an immonium base. In the salts the anthrone nucleus is probably in the enolic form; the acylated salts are of a very similar character.

The further investigation of the remarkable class of free radicals known as the 1-aroyloxanthronyls has led to a modified conception of their nature. These substances, of which 1-*p*-chlorobenzoyloxanthronyl has been investigated in greatest detail, were first obtained by the reduction of 1-aroylanthraquinones with aluminium bronze in sulphuric acid solution. The simplest view of their constitution is that expressed by the formula IX.

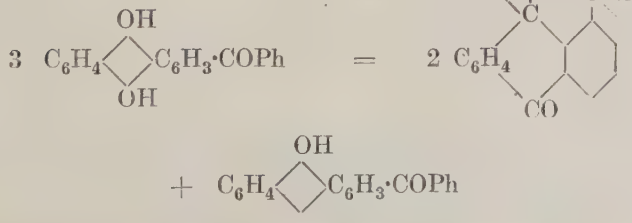
(VIII.) 

 (IX.)

The suggestion which replaces this view is that the hydrogen atom is co-ordinately attached to two oxygen atoms, with the result that the free valency is shared by two carbon atoms as shown in the expression



These substances therefore contain two carbon atoms which are together septavalent.[19] The experimental side of the work scarcely lends itself to summarisation, but a new method of preparation applied to the parent substance of the group may be mentioned. 1-Benzoylanthraquinone is made from the chloride of anthraquinone-1-carboxylic acid and benzene by the action of aluminium chloride and then reduced by zinc dust and glacial acetic acid to 1-benzoylanthraquinol (X). This undergoes what is called "disproportionation" on treatment with hydrochloric acid in accordance with the scheme:

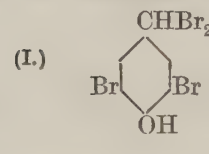
(X.)  (XI.)

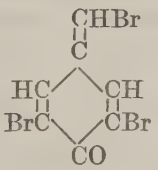
[19] R. Scholl and H. Hähle, *Ber.*, 1923, **56**, [*B*], 918, 1065; *A.*, i, 584, 689.

Benzoyloxanthronyl (XI) occurs in bluish-violet needles, m. p. 192—193°, and exhibits the behaviour of a univalent radical.[20]

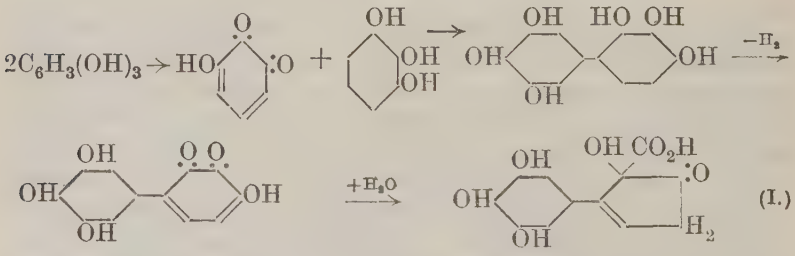
Miscellaneous.

*p-iso*Propylphenylacetaldehyde (incorrectly designated as *p*-cymylacetaldehyde) has been prepared and found to possess a strong odour of vervain.[21] The existence of monomeric quinonehalogenmethides appears to have been definitely proved.[22] The action of phosphorus pentabromide on 3 : 5-dibromo-4-hydroxybenzaldehyde yields the benzylidene bromide (I), which is transformed into 3 : 5-dibromo-

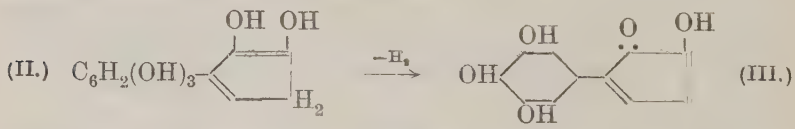




quinonebromomethide (II) by short treatment with cold alcohol or by shaking an ethereal solution with aqueous sodium acetate. This substance is unimolecular, but polymerises rapidly in hot benzene solution. It is hydrolysed with remarkable ease with formation of the original hydroxy-aldehyde. An interesting explanation of the formation of purpurogallin [23] is shown in the scheme given below : [24]

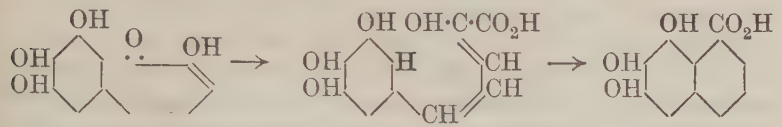


In the first place, a quinonoid addition and in the second a benzil–benzilic acid-type transformation is postulated. The product (I) then loses carbon dioxide and hydrogen, yielding in turn the substance (II) and purpurogallin (III).



[20] R. Scholl, H. Dehnert, and H. Semp, *Ber.*, 1923, **56**, [*B*], 1633; *A.*, i, 807.
[21] L. Bert, *Compt. rend.*, 1923, **177**, 550; *A.*, i, 1101.
[22] H. Lindemann, *Annalen*, 1923, **431**, 270; *A.*, i, 686.
[23] A. G. Perkin, *P.*, 1913, **29**, 354.
[24] R. Willstätter and H. Heiss, *Annalen*, 1923, **433**, 17; *A.*, i, 1212.

The conversion of purpurogallin into purpurogallone is supposed to be due to a second benzilic acid transformation as follows :



The conclusion has been drawn [25] that the isomerism of the "saturated" and "unsaturated" silicohydrocarbons, Si_4Ph_8, produced by the action of sodium on diphenylsilicon dichloride [26] is very probably to be expressed by the formulæ IV and V, respectively.

(IV.) $\begin{matrix} SiPh_2{\cdot}SiPh_2 \\ | \quad\quad | \\ SiPh_2{\cdot}SiPh_2 \end{matrix}$ $-SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2-$ (V.)

In addition to the facts already known in regard to the gap which exists between the reactivities of the isomerides and which have been confirmed and extended by striking new observations, it has been found that the iodide, $Si_4Ph_8I_2$, derived from the unsaturated silicohydrocarbon, reacts with magnesium ethyl bromide with formation of diethyloctaphenylsilicotetrane, $Et_2Si_4Ph_8$. On the other hand, decaphenylsilicotetrane, Si_4Ph_{10}, could not be obtained by an analogous reaction.[27] It seems that there is room for the ethyl groups, but not for phenyl. An intermediate in the formation-reaction of the two silicohydrocarbons is probably $SiPh_2Cl{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2Cl$, and this may lose two chlorine atoms so as to form a ring or, on account of steric hindrance, the compound containing two tervalent silicon atoms.

Cuprous phenyl, CuPh, is obtained as a white powder by the action of magnesium phenyl bromide on cuprous iodide. On warming in benzene solution, it is quantitatively decomposed with formation of diphenyl and a copper mirror.[28]

In closing this series of Reports, it is desired to add an expression of a sense of deep indebtedness to all the colleagues who have lightened an onerous task, and especially to the Abstractors, whose careful summaries of long and often difficult memoirs have greatly facilitated the work, even in the numerous cases where reference to the original was necessary.

R. Robinson.

[25] F. S. Kipping, *T.*, 1923, **123**, 2590.
[26] F. S. Kipping and J. E. Sands, *T.*, 1921, **119**, 830.
[27] F. S. Kipping, *T.*, 1923, **123**, 2598.
[28] R. Reich, *Compt. rend.*, 1923, **177**, 322; *A.*, i, 972.

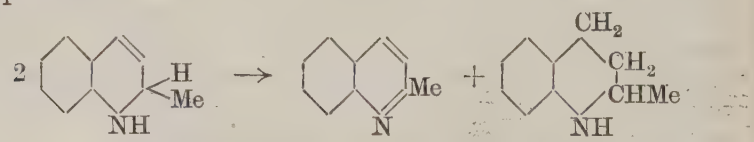
Part III.—Heterocyclic Division.

The volume of work falling within the purview of this Report is somewhat smaller than that dealt with last year, and, with the exception of important papers on morphine and its congeners, includes little of outstanding value. Nevertheless, a number of observations have been made, the collective significance of which would seem distinctly interesting at the present time.

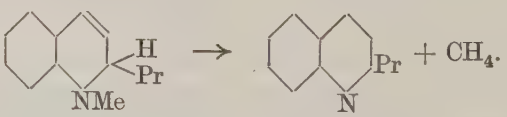
The chemistry of pyrrole derivatives seems now sufficiently complete to encourage the hope that the examination of chlorophyll and hæmoglobin may soon enter on a fresh stage.

Some Conditions of Molecular Stability and Reactivity.

Those theories of organic chemistry which are concerned with molecular structure are founded on the hypothesis that stability is very closely associated with molecular saturation. The corollary of this view that any molecular structure will tend to assume the most saturated condition has not always received the attention it deserves. For example, it seems never to have been suggested that the immediate transition of synthetic dihydroquinaldine into quinaldine and its tetrahydro-derivative in the Doebner and Miller reaction is due to the more saturated character of each of the latter compounds :



Similarly, when 1-methyl-2-propyldihydroquinoline is distilled under atmospheric pressure, it suffers partial decomposition into methane and 2-propylquinoline : [1]

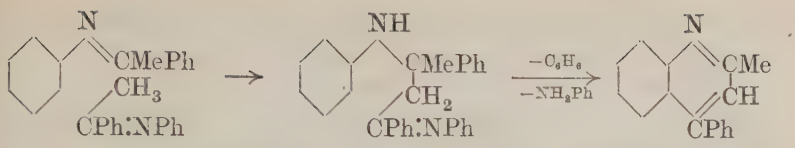


Failure to realise the probability that this might occur was responsible for the erroneous statement that the tetrahydro-derivative prepared from the supposedly pure dihydro-compound could exist in stereoisomeric forms.[2] Again, the hydrochloride of acetophenone-anil is converted at 180° into 4-phenyl-2-methylquinoline : [3]

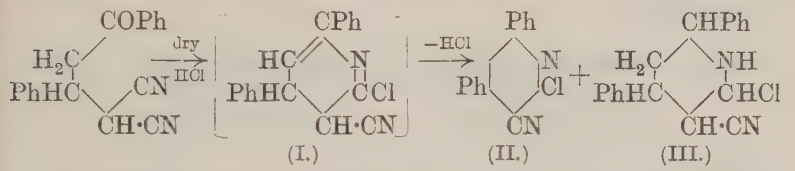
[1] J. Meisenheimer and M. Schütze, *Ber.*, 1923, **56**, [*B*], 1353 ; *A.*, i, 839.

[2] M. Freund and E. Kessler, *J. pr. Chem.*, 1918, [ii], **98**, 233 ; *A.*, 1919, i, 283.

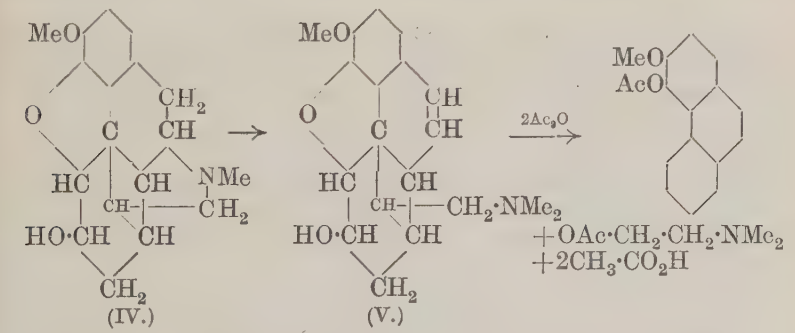
[3] E. Knoevenagel and O. Goos, *Ber.*, 1922, **55**, [*B*], 1929 ; *A.*, 1922, i, 751.



Similar tendencies on the part of dihydropyridine derivatives have frequently been observed, and are discussed in a paper in which it is shown that the pyridine (II) and its hexahydro-derivative (III) are formed in place of the dihydro-compound (I) which would be expected : [4]



It has recently been suggested that the general readiness with which morphine derivatives decompose into derivatives of phenanthrene and of aminoethanol is similarly due to the tendency to produce an aromatic nucleus. The important conclusion, revolutionary in the discussion of the constitution of these alkaloids, has therefore been drawn that the ethanamine grouping must be attached to the nucleus which eventually becomes aromatic at a carbon atom (13 or 14) which is not provided with a hydrogen atom or hydroxyl group. The formulæ (IV) and (V), respectively assigned to codeine and α-methylmorphimethine, illustrate these points.[5]



[4] E. P. Kohler and B. L. Souther, *J. Amer. Chem. Soc.*, 1922, **44**, 2903; *A.*, i, 243.

[5] J. M. Gulland and R. Robinson, *T.*, 1923, **123**, 980. The formation of eudalene when eudesmol or selinene is heated with sulphur (L. Ruzicka, J. Meyer, and M. Mingazzini, *Helv. Chim. Acta*, 1922, **5**, 349; *A.*, 1922, i, 560; *Ann. Reports*, 1922, **19**, 118) involves the extrusion of a methyl group due to a similar cause.

The same paper contains a discussion of yet other modes in which the same fundamental tendency manifests itself.[6]

A familiar process by which the molecules of unsaturated compounds tend to become more saturated is that of more or less well-defined association with other unsaturated molecules. It was pointed out in a previous Report[7] that in such cases four-membered rings are frequently formed and that, from the kinetic point of view, a reaction between two molecules is more likely to occur than one between three. In agreement with this, dimethindiazidines, for example (I), have been prepared by direct combination of azomethines :

$$\begin{matrix} HO\cdot C_6H_4\cdot CH{:}NPh \\ + \\ C_6H_4Br\cdot N{:}CHPh \end{matrix} \longrightarrow \begin{matrix} HO\cdot C_6H_4\cdot CH\cdot NPh \\ | \quad | \\ C_6H_4Br\cdot N{-}CHPh \end{matrix} \quad (I.)$$

In other cases, the formation of such an intermediate product is the most plausible explanation of the attainment of an equilibrium which can be reached from either side.[8] For example,

$$m\text{-}NO_2\cdot C_6H_4\cdot CH{:}NPh + CHPh{:}N\cdot C_6H_4Br(p) \rightleftarrows \text{diazidine} \rightleftarrows m\text{-}NO_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4Br(p) + CHPh{:}NPh.$$

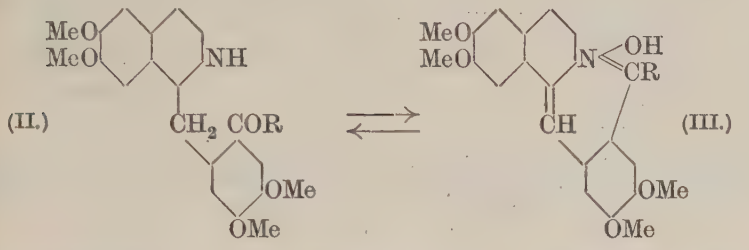
In another instance,[9] the symmetrical dimeric form is stable at low temperatures, and is only completely broken down at 250° :

$$\begin{matrix} CH_2\cdot N\cdot C_6H_4Me \\ | \quad | \\ C_6H_4Me\cdot N{-}CH_2 \end{matrix} \rightleftarrows 2CH_2{:}N\cdot C_6H_4Me.$$

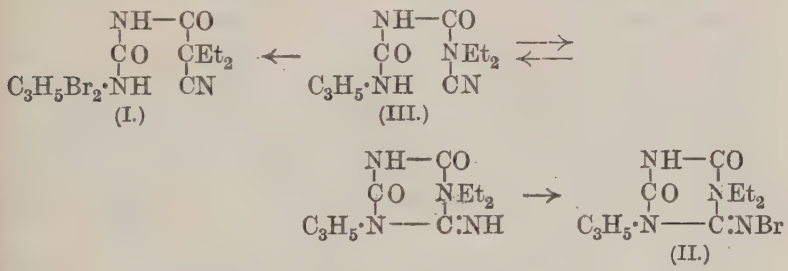
In all such cases the resulting equilibrium represents, if the influence of surrounding media be for the moment neglected, a compromise between the tendency towards more complete saturation and instability of the resulting ring structure, just as tautomerism may be due to an equilibrium between two conditions of equal molecular saturation or between one of greater saturation and some particular source of instability inherent in that condition.[10] Some interesting observations have been made during the year which would seem to fall in this category. Acetylpapaverine (R = Me in II) has a considerable tendency to pass into the ammonium base, coralyne (R = Me in III), but aqueous solutions of

[6] Compare, for example, p. 992.
[7] *Ann. Reports*, 1920, **17**, 97.
[8] C. K. Ingold and H. A. Piggott, *T.*, 1922, **121**, 2793.
[9] *Idem*, *T.*, 1923, **123**, 2745.
[10] F. Allsop and J. Kenner, *ibid.*, p. 2306.

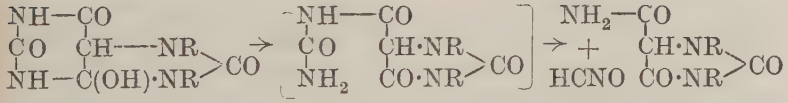
homocoralyne, on the other hand, are very unstable and gradually deposit propionylpapaverine : [11]



The formation of the products (I) and (II) by bromination of allylveronal [12] suggests that this and the open-chain compound (III) are ring-chain tautomerides :

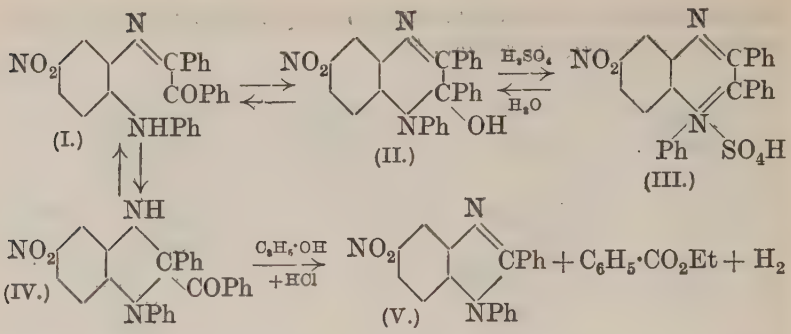


The result of the decomposition by heat of 4-hydroxy-7 : 9-dialkyl-4 : 5-dihydrouric acid [13] points to a similar conclusion :



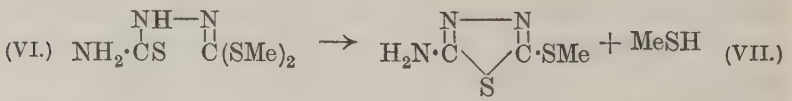
A reaction interesting from some of the above points of view occurs when 4-nitro-2-aminodiphenylamine is treated with benzil. The stilbazonium derivative usually obtained from such condensations is also obtainable in this case as a sulphate (III), if a solution of the intermediate anil (I) in concentrated sulphuric acid be cautiously diluted with water; excessive dilution, however, causes separation of the original anil, although the ψ-base (II) is precipitated from solutions of the salts on addition of ammonia. The following equilibrium therefore apparently exists :

[11] W. Schneider and E. Nitze, *Ber.*, 1923, **56**, [*B*], 1036; *A.*, i, 701.
[12] O. Diels, *Annalen*, 1923, **432**, 115; *A.*, i, 950.
[13] H. Biltz and R. Lemberg, *ibid.*, p. 137; *A.*, i, 955.



But the anil also has a slight tendency to form the derivative (IV). The stability of such dihydrobenziminazoles would, however, seem to be slight in comparison with that of the benziminazoles (for example, these have so far resisted attempts at direct reduction to dihydro-derivatives) and consequently when the anil (I) is boiled with alcoholic hydrochloric acid, the products are not stilbazonium salts, but 5-nitro-1 : 2-diphenylbenziminazole (V) and ethyl benzoate, arising from the irreversible reaction indicated. The result depends on the very slight basicity of the stilbazonium hydroxide, and therefore is not observed when 4-chloro-2-aminodiphenylamine or 4-nitro-*o*-phenylenediamine is treated with benzil.[14]

Saturation as above considered is one form of what has been termed "chemical neutralisation," which was mentioned in last year's Report [15] in connexion with the formation of cyclic compounds from hydrazodicarbon-mono- and -di-thiocarbonamides under the influence of alkali or acid. A more extended investigation of this question [16] has revealed some exceptions to the suggestion that these alkaline or acidic reagents respectively give rise to the formation of acidic or basic products. Thus methyl thiosemicarbazidedithiocarbonate (VI) furnishes 2-amino-5-methylthiol-1 : 3 : 4-thiodiazole (VII), whether it be heated alone or treated with either acid or alkali :



The explanation is that in general such reactions occur in two stages; the first consists in the removal of, for example, ammonia

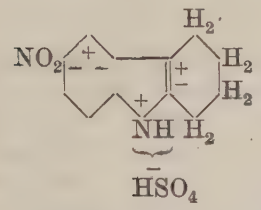
[14] K. Brand and E. Wild, *Ber.*, 1923, **56**, [*B*], 105; *A.*, i, 251.

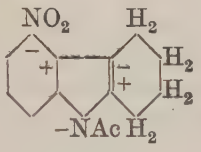
[15] *Ann. Reports*, 1922, **19**, 130.

[16] F. Arndt and F. Bielich, *Ber.*, 1923, **56**, [*B*], 2276; *A.*, 1924, i, 22; E. Fromm, *Annalen*, 1923, **433**, 1; *A.*, i, 1239.

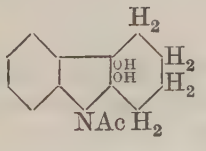
or, as in the example quoted, methyl mercaptan, whilst in the second, internal condensation of the unsaturated compound occurs according to the above-mentioned suggestion, when alternatives are open. In certain cases, however, only one course is possible, and the result may then be at variance with the view indicated.

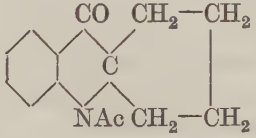
The underlying idea of the theory of induced alternate polarity is clearly also one of neutralisation. An interesting application of this theory has been made to explain the formation of (I) and (II) by the nitration respectively of tetrahydrocarbazole in concentrated sulphuric acid solution and of its *N*-acetyl derivative.

(I.) 

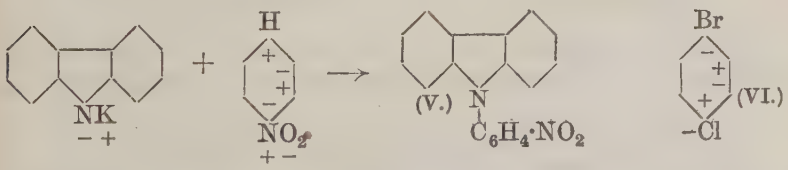
 (II.)

The justification for considering the orienting influences to be transmitted in the manner indicated by the signs of polarity, rather than more directly through the aromatic nucleus, lies in the observation that the ethylenic linking in tetrahydrocarbazole is specially reactive. For example, the pinacol (III) is obtainable under certain conditions of nitration, and, it may be noted, passes into the *spiro*-compound (IV) when heated alone or with acetic anhydride.[17]

(III.) 

 (IV.)

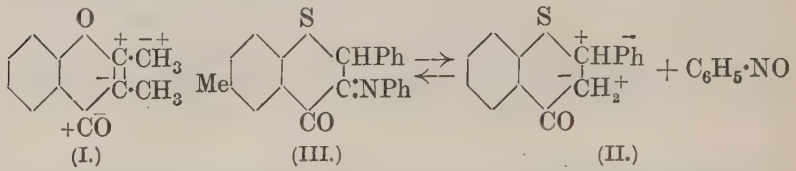
Another reaction, noteworthy from the same point of view, consists in the formation of *N*-*p*-nitrophenylcarbazole (V) by heating potassium carbazole with the usually inert nitrobenzene at the low temperature of 45—50° :



The result becomes perhaps more significant by contrast with the

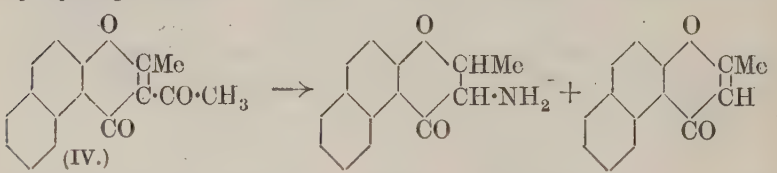
[17] W. H. Perkin and S. G. P. Plant, *T.*, 1923, **123**, 676.

fact that the analogous synthesis of *p*-chlorophenylcarbazole, by the aid of *p*-chlorobromobenzene (VI), requires a temperature of 210°.[18] The reactivities of the 2-methyl group in 2 : 3-dimethylchromone (I)[19] and of the 3-hydrogen atoms in 6-methylthiochromone and -flavanone (II) are also readily interpreted in terms of the theory of polarity.



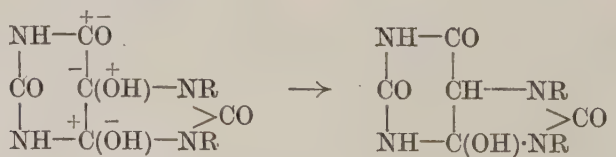
(I.) (III.) (II.)

The hydrolysis of the condensation product (III) of the thioflavanone with nitrosobenzene to the original compounds rather than to aniline and the corresponding diketone is very striking. The polar effect of the phenyl group is alone indicated in (II), because it is this, superimposed on those of the other atoms, which determines this result. Thus, the diketone is obtainable from methylthiochromanone by the method under discussion.[20] Again, when 3-acetyl-2-methylnaphthachromone (IV) and analogous compounds are treated with alkali, the "positive" acetyl group is replaced by hydrogen :[21]



(IV.)

In yet another direction, 4-hydroxy-7 : 9-dialkyl-4 : 5-dihydrouric acids are obtained when the corresponding glycols are heated with phosphorus tribromide :



A review of reactions of this type leads to the conclusion that phosphorus trihalides react with enolic hydroxyl preferentially in

[18] G. and M. de Montmollin, *Helv. Chim. Acta*, 1923, **6**, 94; *A.*, i, 373.

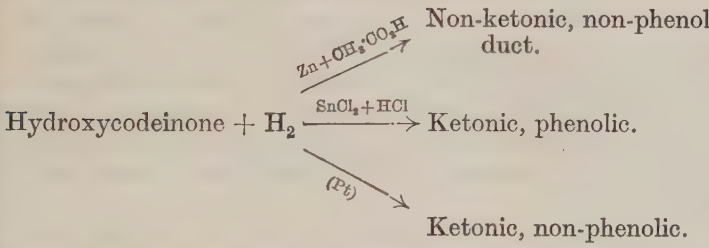
[19] I. M. Heilbron, H. Barnes, and R. A. Morton, *T.*, 1923, **123**, 2559.

[20] F. Arndt and others, *Ber.*, 1923, **56**, [*B*], 1269; *A.*, i, 826; F. Krollpfeiffer and H. Schultze, *ibid.*, p. 1819; *A.*, i, 1113.

[21] W. Schneider and (Miss) H. Bode, *ibid.*, p. 1042; *A.*, i, 699; St. v. Kostanecki and A. Rozycki, *Ber.*, 1901, **34**, 102; *A.*, 1901, i, 222.

such a manner as to replace it by hydrogen. Correspondingly, the chlorine atom of 5-chloro-ψ- or *-iso*-uric acids, or of 5-chloro-4-hydroxydihydrouric acids exhibits "positive" properties.[22] The formation of 2-bromoglyoxaline from 2 : 5-dibromo-4-carboxy-*p*-bromoanilide (p. 143) would seem to be another reaction of this kind.

Valuable as these points of view are, however, they must be regarded only as approximations to the fundamental principle of maximum entropy, and it is not difficult to find examples which suggest that the reactions of organic chemistry will be properly understood only when a more exact application of this principle becomes possible. The various results obtained by reducing hydroxycodeinone [23] illustrate this point :

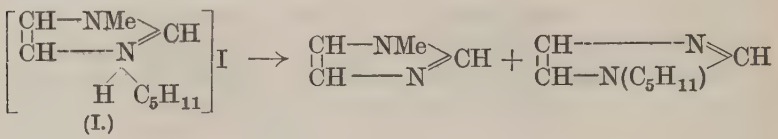


Again, 2-bromothiophen, resulting from the action of cyanogen bromide on thiophen, is probably accompanied by some 2-cyanothiophen,[24] so that the cyanogen bromide apparently does not react according to a perfectly definite distribution of polarity. There are similar indications that absolute rules cannot be laid down in regard to the relative strengths of attachment of groups to the same atom. As is well known, much attention has been bestowed on this question in recent years, and a survey [25] of the results obtained in a variety of directions points to the definite conclusion that aliphatic groups are more easily detached than aromatic. The exact opposite is, however, observed in the reaction of acetophenoneanil already referred to, whilst, among open-chain compounds, the mode of dehydration of glycols, involving ultimate detachment and migration of groups, varies with the conditions employed : [26]

$$\begin{matrix} R \\ Ar \end{matrix}\!>\!CH\cdot COR \xleftarrow[\text{conc. } H_2SO_4]{\text{cold}} HO\cdot CR_2\cdot CHAr\cdot OH \xrightarrow[\text{dilute acid}]{\text{heat or}} R_2CAr\cdot CHO.$$

[22] H. Biltz and R. Lemberg, *Annalen*, 1923, **432**, 137; *A.*, i, 955.
[23] Compare E. Speyer, *ibid.*, 1923, **430**, 1; *A.*, i, 127.
[24] W. Steinkopf, *ibid.*, p. 78; *A.*, i, 124.
[25] J. v. Braun and K. Moldaenke, *Ber.*, 1923, **56**, [*B*], 2165; *A.*, i, 1193.
[26] M. Tiffeneau and (Mlle) J. Lévy, *Bull. Soc. chim.*, 1923, [iv], **33**, 735; *A.*, i, 788.

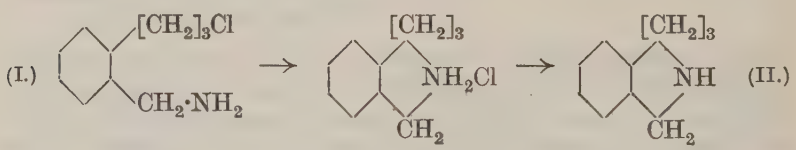
In this connexion, a paper may be noted in which the results of heating various alkyliodides of 1-methylglyoxaline at 260—300° are communicated. For example, 1-methylglyoxaline *iso*amyliodide (I) furnishes equal quantities of *iso*amyl- and methylglyoxalines, but the latter alone results when the benzylbromide derivative is heated : [27]



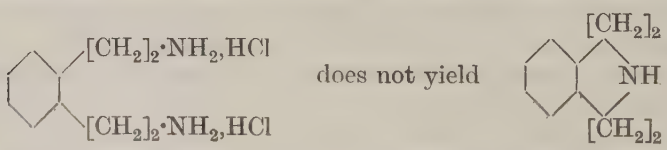
(I.)

Ring Formation.

When the hydrochloride of *o*-γ-chloropropylbenzylamine (I) is heated at 100° with dilute sodium hydroxide solution for a short time, a base, most probably homo*iso*quinoline (II), is obtained. The result is perhaps attributable to the readiness with which, in the first place, irreversible internal quaternary ammonium chloride formation occurs, even during the possibly infrequent phases in which the molecule assumes a configuration favourable to such a reaction :



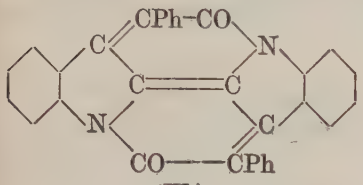
By contrast, a reaction of more complex character does not take place between two amino-groups in the same relative position : [28]



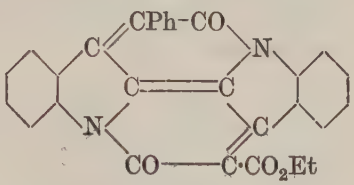
The formation of 4-ketotetrahydro-1 : 5-heptabenzthiazine (III) by heating β-*o*-aminophenylthiolpropionic acid would also seem to illustrate the influence of internal salt formation as an aid to the synthesis of large ring structures : [29]

[27] J. Sarasin, *Helv. Chim. Acta*, 1923, **6**, 370; *A.*, i, 710.
[28] J. v. Braun and F. Zobel, *Ber.*, 1923, **56**, [*B*], 690; *A.*, i, 371.
[29] F. Mayer and C. Horst, *ibid.*, p. 1415; *A.*, i, 844.

Whereas the condensation of indigotin with phenylacetyl chloride yields Lake Red Ciba B (IV), only one molecular proportion of ethyl malonate can be condensed with indigotin. Nevertheless, the product is converted by treatment with phenylacetyl chloride into (V).[30]



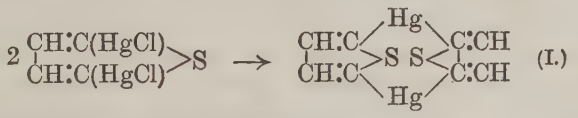
(IV.)



(V.)

Five-membered Heterocyclic Structures.

In some respects, the thiophens are intermediate between the olefines and the benzenes. Thus, usually only additive products are obtained by the action of reagents on olefines, whereas, although those of bromine and of mercuric chloride with thiophens may be isolated in certain cases, they readily pass into substitution derivatives, such as are alone obtained from benzene. On the other hand, cyanogen bromide only reacts with benzene and naphthalene above 200°, and not at all with unsaturated compounds like ethyl fumarate or ethyl cinnamate, but thiophens are easily converted by this reagent into 2-bromo-derivatives, accompanied by small amounts of the corresponding nitriles. 2 : 5-Derivatives of thiophen are only attacked with difficulty by this reagent. The superior reactivity of the α- over the β-position in thiophen is also illustrated by the fact that 2 : 5-dimethyl- and -diphenyl-thiophens alone of the 2 : 5-derivatives examined, form thienyl mercurichlorides, and react relatively slowly.[31] 2 : 2′-Mercurydithienyls have been prepared by treating the corresponding mercurichlorides with sodium stannite, sodium iodide, or sodium thiocyanate.



(I.)

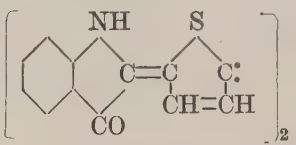
The formation of the cyclic compound (I) from 2 : 5-thienylene-dimercurichloride is the more interesting, since scarcely any cyclic mercuric compounds have been previously prepared.[32]

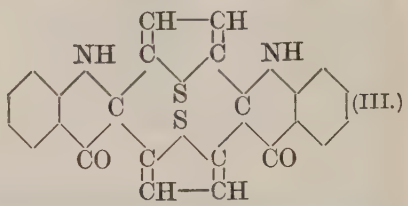
[30] Society of Chemical Industry, Basel, D.R.-P. 260243 of 1913; T. Posner and G. Pyl, *Ber.*, 1923, **56**, [*B*], 31; *A.*, i, 252.

[31] W. Steinkopf, *Annalen*, 1923, **430**, 78; *A.*, i, 124.

[32] W. Steinkopf, W. Bielenberg, and H. Augestad-Jensen, *ibid.*, p. 41; *A.*, i, 125

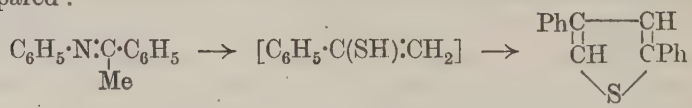
Only thiophens with two free α-positions exhibit the indophenine reaction. Since, further, the analogous condensation product of thiophen with ethyl mesoxalate has a bimolecular formula, the constitution (II) has been assigned to indophenine. The alternative formula (III) does not accord with the indigoid character of indophenine, or with the formation of 2 : 2′-dithienyl from thiophen and sulphuric acid.[33]

(II.) 


(III.)

Biphenylene sulphide, found in coal tar, has not hitherto been easily accessible by synthesis, but it can now be readily prepared by boiling diphenyl sulphoxide in toluene solution with sodamide.[34]

When acetophenoneanil is fused with sulphur at 240°, 2 : 4-diphenylthiophen is obtained, and selenophens may be similarly prepared : [35]



The development of general methods for the preparation of various types of substituted pyrroles has continued. Amino-derivatives, hitherto unknown, have been obtained by hydrogenation of cold alkaline alcoholic solutions of suitable benzeneazopyrroles in presence of platinum. Although the products are strong bases, 4-amino-2 : 3 : 5-trimethylpyrrole, which alone was examined in these respects, did not react with phenylcarbimide, or acid chlorides, and could not be methylated.[36]

Cyanopyrroles also had not previously been prepared, but are readily obtainable from oximes [37] of the aldehydopyrroles, whilst treatment of their hydrazones or semicarbazones with sodium ethoxide in the usual manner provides a convenient source of alkylpyrroles.[38] The failure to obtain phyllopyrrole from 3-aceto-5-aldehydo-2 : 4-dimethylpyrrole is an isolated exception to this

[33] W. Schlenk and (Miss) O. Blum, *Annalen*, 1923, **433**, 95; *A.*, i, 1235.

[34] A. Schönberg, *Ber.*, 1923, **56**, [*B*], 2275; *A.*, 1924, i, 39.

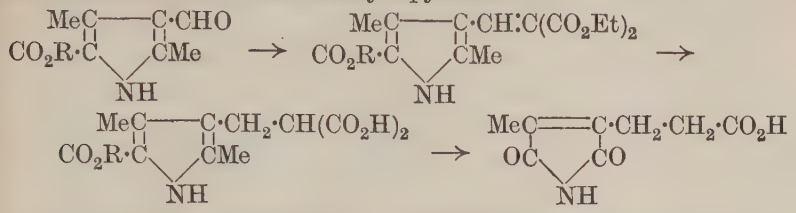
[35] M. T. Bogert and P. P. Herrera, *J. Amer. Chem. Soc.*, 1923, **45**, 238; *A.*, i, 240.

[36] H. Fischer and F. Rothweiler, *Ber.*, 1923, **56**, [*B*], 512; *A.*, i, 391.

[37] H. Fischer and W. Zerweck, *ibid.*, p. 519; *A.*, i, 364.

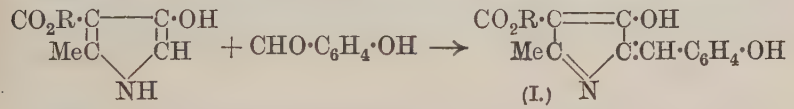
[38] H. Fischer and M. Schubert, *ibid.*, p. 1202; *A.*, i, 707; H. Fischer, B. Weiss, and M. Schubert, *ibid.*, p. 1194; *A.*, i, 703.

statement.[39] A new synthesis of hæmatic acid also depends in the first place on that of an aldehydopyrrole :[40]

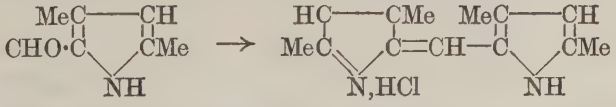


In view of this importance of aldehydopyrroles, the successful application of Gattermann's synthesis to *N*-methyl- and *N*-phenyl-pyrroles is noteworthy.[41]

The object of all this work is of course the perfection of methods permitting closer inquiry into the manner in which the various well-recognised alkylated pyrrole nuclei are united in the molecular structure of biologically important pigments. Bilirubin, which from its oxidation to hæmatic acid is known to contain a pyrrole nucleus, has now been shown [42] to contain, not a methylimino-group, but an imino-group, which undergoes methylation when this dibasic acid is esterified by means of diazomethane.[43] Since this behaviour is reproduced by the pyrrolenyl derivative (I) (although not by the analogous furfurylidene derivative), of which the synthesis is indicated, it is concluded that bilirubin contains a



pyrrolenyl nucleus connected with a pyrrole nucleus through a single carbon atom. Bilirubic acid, obtained from the pigment by reductive degradation, had already been formulated as an unsymmetrical methene conforming to this description. Compounds of this type [44] have now been prepared by the action of hot dilute mineral acid on 2-aldehydopyrroles,[45]



[39] H. Fischer and H. Ammann, *Ber.*, 1923, **56**, 2319; *A.*, 1924, i, 78.

[40] W. Küster and H. Maurer, *ibid.*, p. 2478.

[41] H. Fischer and K. Smeykal, *ibid.*, p. 2368.

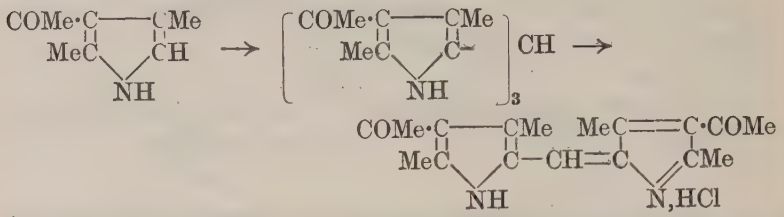
[42] W. Küster and W. Maag, *ibid.*, p. 55; *A.*, i, 242.

[43] Compare W. Küster and others, *Z. physiol. Chem.*, 1915, **94**, 136; *A.* 1915, i, 829.

[44] H. Fischer, *Ber.*, 1912, **45**, 1979; O. Piloty and Thannhauser, *ibid.* p. 2393; *A.*, 1912, i, 646, 925.

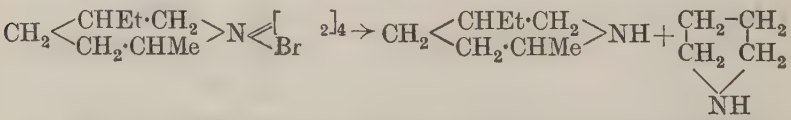
[45] H. Fischer and W. Zerweck, *loc. cit.*

or on the tripyrrylmethanes (obtained when the pyrroles are subjected to the Reimer-Tiemann reaction) : [46]



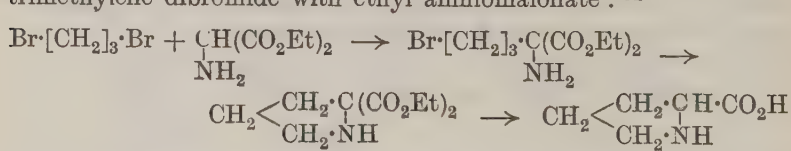
As a further step, these and other dipyrrylmethenes have been shown to furnish complex copper, zinc, and nickel, but not ferric, salts, in which the atom of the metal is united to two pyrrole nuclei by principal and to two pyrrolenyl nuclei by subsidiary valencies. The copper salts resemble that of mesobilirubinogen in exhibiting three absorption bands, whilst the zinc complex salts show a fluorescence corresponding to that of urobilin.[47]

The thermal decomposition of cyclic bisimines [48] has been applied to the preparation of pyrrolidine by heating the quaternary ammonium bromide prepared from 1 : 4-dibromobutane and the now easily accessible copellidine [49] (using preferably the stereoisomeride which furnishes the less soluble hydrochloride) for twenty-four hours with ammonia at 170—180° : [50]



The interval of 80° between the boiling points of pyrrolidine and copellidine renders their separation easy.

A new synthesis of proline depends on the condensation of trimethylene dibromide with ethyl aminomalonate : [51]



[46] H. Fischer and H. Ammann, *loc. cit.*; compare O. Piloty, W. Krannich, and H. Will, *Ber.*, 1914, **47**, 2531; *A.*, 1915, i, 461; H. Wiedmann, *Diss.*, Munich, 1920.

[47] H. Fischer and M. Schubert, *Ber.*, 1923, **56**, [*B*], 2379.

[48] Compare *Ann. Reports*, 1922, **19**, 127.

[49] Höchster Farbwerke, D.R.-P. 347820, 349184, 349267.

[50] J. v. Braun, G. Lemke, and (Miss) A. Nelken, *Ber.*, 1923, **56**, [*B*], 1564; *A.*, i, 840.

[51] N. J. Putochin, *ibid.*, p. 2213; *A.*, i, 1225.

The Gattermann and Hoesch syntheses have been successfully applied to 2-methyl- and 2-carbethoxy-indoles, but indole itself is not reactive.[52]

The discussion of the alleged cases of isomerism in the isatin series has been continued. Thus, it is claimed that to the isomeric forms of isatin and 4-hydroxyquinaldine, two forms of ketodihydroindazole correspond,[53] but at the same time it is admitted that the alleged isomerides are polymolecular in various solvents, including phenol. This result is ascribed to association, but it has been very pertinently objected that such a view is inapplicable when hydroxylic solvents are concerned, and that the compounds in question are in reality polymerides of the simple compounds.[54]

The formulation of the supposed isomeric forms of ethyl isatogenate as an additive compound with ethyl alcohol [55] has been accepted and confirmed by analysis, but at the same time the existence of isomerides of carbethoxy- and nitro-phenylisatogen is affirmed, and in the latter case it is shown that an additive compound with ethyl alcohol can also be obtained under somewhat different experimental conditions.[56]

The preparation of *peri*naphthindigotin has now been achieved,[57] and in two papers [58] the identity of α- and β-indines with *iso*indigotin is independently demonstrated.

Ethylene oxalate decomposes at 240° largely into ethylene and carbon dioxide, but also to a considerable extent into ethylene carbonate and carbon monoxide :

$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + 2CO_2 \xleftarrow{40\,\%} \begin{matrix}CH_2\cdot O\cdot CO\\ |\quad\quad |\\ CH_2\cdot O\cdot CO\end{matrix} \xrightarrow{23\,\%} \begin{matrix}CH_2\cdot O\\ |\\ CH_2\cdot O\end{matrix}\!\!>CO + CO.$$

Other products include acetaldehyde.[59]

It has not been possible to synthesise optically active forms of the ketothiazolidines (I) or of the rhodanines (II) owing to their tendency to enolisation. In the case of the diketothiazolidines (III), however, this tendency is sufficiently restrained to permit optical

[52] R. Seka, *Ber.*, 1923, **56**, [*B*], 2058; *A.*, i, 1125; H. Fischer and K. Pisbor, *ibid.*, p. 2313; *A.*, 1924, i, 86.

[53] G. Heller and W. Köhler, *ibid.*, p. 1595; *A.*, i, 850.

[54] A. Hantzsch, *ibid.*, p. 2110; *A.*, i, 1226.

[55] Compare *Ann. Reports*, 1922, **19**, 135.

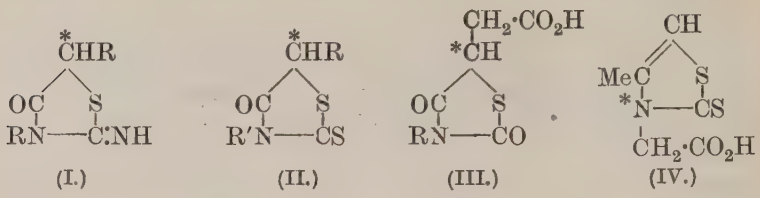
[56] P. Rüggli, A. Bolliger, and W. Leonhardt, *Helv. Chim. Acta*, 1923, **6**, 594; *A.*, i, 833.

[57] S. Dutt, *T.*, 1923, **123**, 224; compare *Ann. Reports*, 1922, **19**, 131.

[58] A. Wahl and W. Hansen, *Compt. rend.*, 1923, **176**, 1070; *A.*, i, 607; O. Dornier and Jh. Martinet, *Bull. Soc. chim.*, 1923, **33**, 779; *A.*, i, 852.

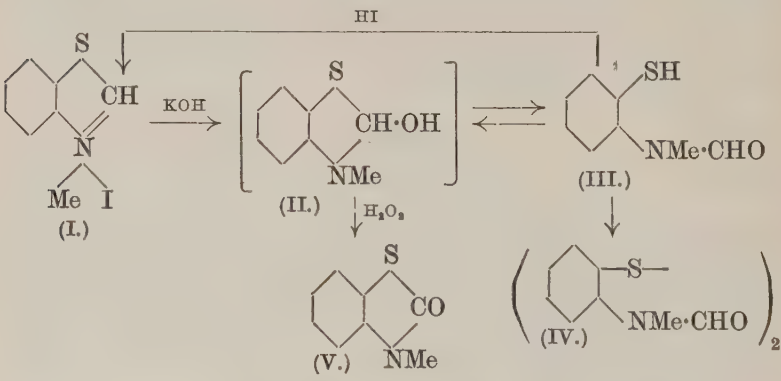
[59] M. Tilitschéev, *Ber.*, 1923, **56**, [*B*], 2218; *A.*, i, 1173.

activity to be observed when the synthetic products are isolated with sufficient rapidity.[60]



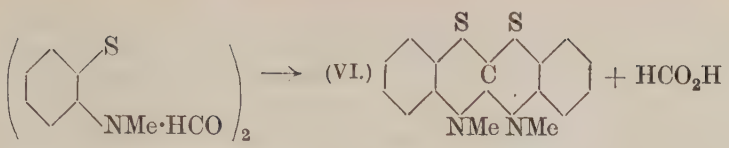
Stereochemical considerations have also led to the synthesis of another thiazole derivative (IV). The failure of all attempts to resolve this compound into optically active components [61] accords with the considered opinion of one of the foremost workers on the subject of asymmetric tervalent nitrogen that "the asymmetric saturated tervalent nitrogen atom can give rise only in very special cases, if ever, to the existence of stereoisomerides." [62]

The ψ-base derived from benzothiazole methiodide (I) is not the carbinol (II), but the monobasic acid (III), which is reconvertible into salts of the true benzothiazole base by treatment with acid, and is also easily oxidised by iodine or alkaline ferricyanide to the disulphide (IV): [63]

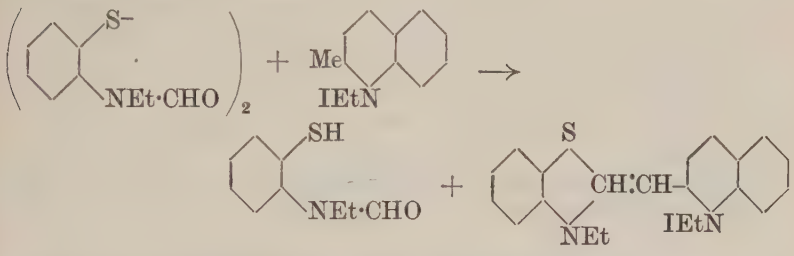


Evidence that (II) is an intermediate product in the above change is obtained by the formation of small amounts of methylbenzothiazolone (V) when the methiodide is treated with alkaline hydrogen peroxide. When the disulphide is heated with phenylhydrazine, the asymmetric bis-2-methylbenzothiazoline-1 : 1-spiran (VI) is

[60] S. Kallenberg, *Ber.*, 1923, **56**, [*B*], 316; *A.*, i, 247.
[61] B. Groth and B. Holmberg, *ibid.*, p. 289; *A.*, i, 246.
[62] J. Meisenheimer and M. Schütze, *ibid.*, p. 1353; *A.*, i, 839.
[63] W. H. Mills, L. M. Clark, and J. A. Aeschlimann, *T.*, 1923, **123**, 2353.

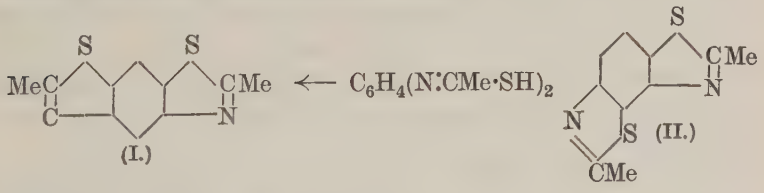


produced. If, in place of the hydrazine, an alkyl salt of a base containing a reactive methylene group be employed, the latter reacts with the formic acid to produce carbocyanines and similar dyestuffs. Thus, in the case of ethylquinaldinium nitrate and di-*o*-formylethylaminodiphenyl disulphide, pinacyanol is produced. At the same time, however, another reaction occurs with formation of dyes of the *iso*cyanine type : [64]



Similar results are obtained when 1-methylbenzothiazole ethiodide, lepidine ethonitrate, or 4-phenyl-2-methylthiazole methiodide is employed.[65]

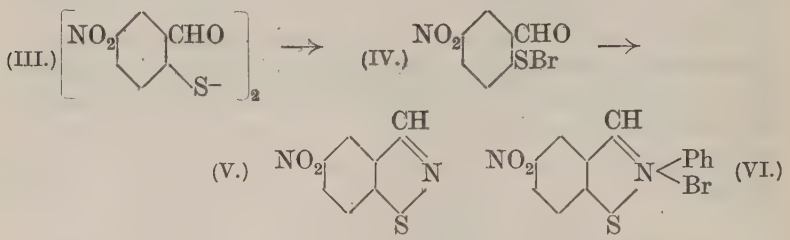
2 : 6-Dimethylbenz*bis*thiazole (I) has been prepared from the dithioacetyl derivative of *m*-phenylenediamine by oxidation with alkaline potassium ferricyanide solution :



The formula (I) is preferable to (II) because the actual product is readily formed, and yields a monomethiodide in the same manner as the product obtained from 2 : 6-diaminotoluene, which necessarily corresponds to (I), whereas the product from 2 : 4-diaminotoluene, which must be of the type (II), is much less readily formed, and furnishes a dimethiodide. There is an indication, however, that a small proportion of (II) accompanies (I).[66]

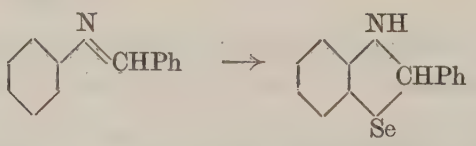
[64] W. H. Mills, L. M. Clark, and J. A. Aeschlimann, *T.*, 1923, **123**, 2362.
[65] W. H. Mills and W. T. K. Braunholtz, *ibid.*, p. 2804.
[66] S. R. H. Edge, *T.*, 1922, **121**, 772; 1923, **123**, 153, 1011.

Derivatives of benzo*iso*thiazole have been prepared for the first time from 2-chloro-5-nitrobenzaldehyde. The disulphide (III), obtained from this compound by treatment with sodium sulphide, is converted by prolonged treatment with bromine into the bromide (IV), which yields 5-nitrobenz-4′ : 5′-*iso*thiazole (V) when boiled in benzene solution with concentrated aqueous ammonia solution :



The salt (VI) is produced if aniline be employed in place of ammonia.[67]

2-Phenylbenzoselenazole is best prepared by boiling benzylideneaniline with selenium : [68]



Although it is now well recognised that many heterocyclic aminocompounds are diazotisable, the value of the reaction for synthetic purposes is frequently very limited. Thus, 4-iodo-3 : 5-dimethylpyrazole is much more conveniently prepared by direct substitution than from the diazonium compound.[69] Again, aminomethylfurazan, when diazotised, at once furnishes the diazoaminocompound.[70]

Substitution of bromine for hydrogen in 4-methylglyoxaline occurs first in the 5- rather than in the 2-position, because the monobromo-derivative obtained differs from that prepared by brominating ethyl 4-methylglyoxaline-5-carboxylate and subsequently removing the carboxyl group.[71] Bromination of glyoxaline-5-carboxyanilide also occurs first in the 4-position, but 2-bromo-

[67] K. Fries and G. Brothuhn, *Ber.*, 1923, **56**, [*B*], 1630; *A.*, i, 842.

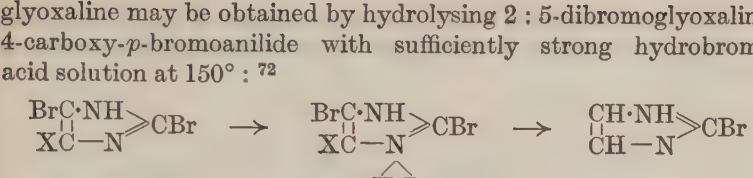
[68] M. T. Bogert and Yü-Gwan Chen, *J. Amer. Chem. Soc.*, 1922, **44**, 2352; *A.*, 1922, i, 1182.

[69] G. T. Morgan and I. Ackerman, *T.*, 1923, **123**, 1308.

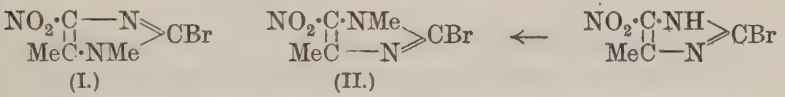
[70] G. Ponzio and G. Ruggeri, *Gazzetta*, 1923, **53**, i, 297; *A.*, i, 853.

[71] F. L. Pyman and G. M. Timmis, *T.*, 1923, **123**, 494.

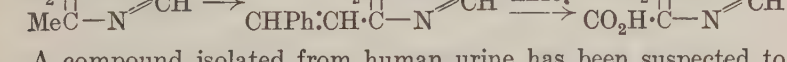
glyoxaline may be obtained by hydrolysing 2 : 5-dibromoglyoxaline-4-carboxy-*p*-bromoanilide with sufficiently strong hydrobromic acid solution at 150° : [72]



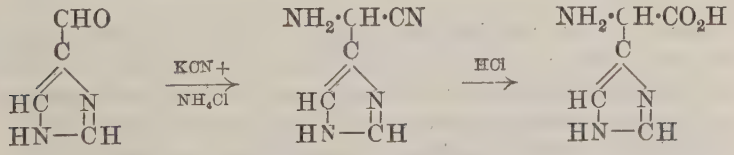
2 : 5-Dibromoglyoxaline may be obtained under milder conditions of hydrolysis. Although there is no statement as to whether this is similarly convertible into the 2-bromo-compound, the reaction by which this is produced may probably be compared with the displacement of iodine from *o*- and *p*-iodoanilines by means of acid.[73] This analogy between reactions of glyoxaline and benzene derivatives is clearly seen in the ready conversion of 4-nitro-1 : 5-dimethylglyoxaline into a 2-bromo-derivative (I), as contrasted with the non-formation of (II) by similar procedure.



In (II), which can be prepared by alkylation in the manner indicated, the bromine atom occupies a para-position with respect to the nitro-group, and therefore is mobile, whilst in (I) the meta-orientation of the bromine atom and the nitro-group involves the non-reactivity of the halogen atom.[74] Again, 5-nitro-4-methylglyoxaline resembles the nitrotoluenes in its reactivi y towards benzaldehyde, which provides a very satisfactory method of preparing 5-nitroglyoxaline-4-carboxylic acid : [75]

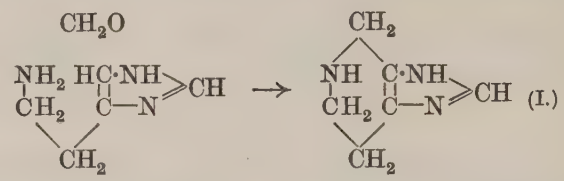


A compound isolated from human urine has been suspected to be 4-glyoxalylaminoacetic acid,[76] and this view has been substantiated by the synthesis of this lower homologue of histidine : [77]

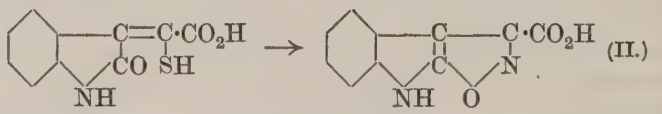


[72] H. King and W. O. Murch, *T.*, 1923, **123**, 621.
[73] Compare *Ann. Reports*, 1922, **19**, 100.
[74] F. L. Pyman and G. M. Timmis, *loc. cit.*
[75] A. Windaus and W. Langenbeck, *Ber.*, 1923, **56**, [*B*], 683; *A.*, i, 386.
[76] R. Engeland, *Z. physiol. Chem.*, 1908, **57**, 49; *A.*, 1908, ii, 1056.
[77] C. P. Stewart, *Biochem. J.*, 1923, **17**, 130; *A.*, i, 486.

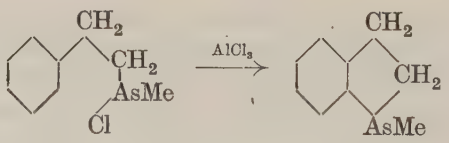
β-Glyoxalyl*iso*piperidine (I) has been obtained by the gradual addition of methylal to a solution of 4-β-aminoethylglyoxaline at 100° : [78]



Indo*iso*oxazole-γ-carboxylic acid (II), prepared by the action of hydroxylamine on oxindole-3-α-thiolacetic acid, is the first instance of a compound in the molecule of which indole and oxazole rings are fused together : [79]

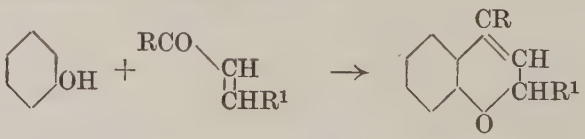


A preliminary account has been given of the formation of *As*-methyldihydroarsindole from β-phenylethylmethylchloroarsine : [80]



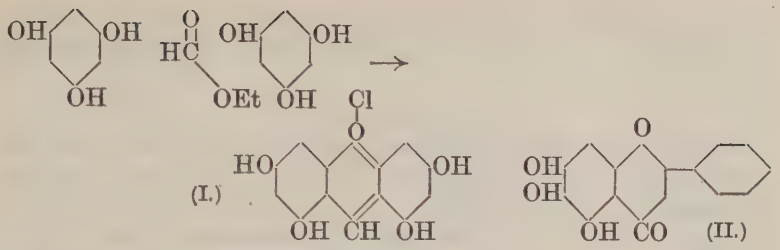
The Pyrone Group.

2 : 4-α-Chromenes have been obtained by condensing phenols with αβ-unsaturated ketones : [81]



As usual in such reactions, resorcinol and *m*-dimethylaminophenol give more favourable results than the simple phenols. Similarly, phloroglucinol condenses remarkably easily with ethyl formate or ethyl orthoformate in presence of hydrogen chloride to form the xanthylium salt (I), but simpler phenols react less readily : [82]

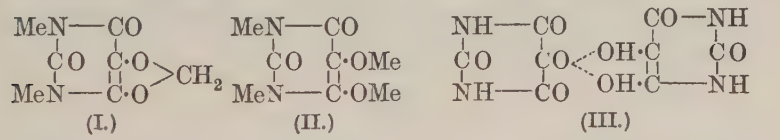
[78] Society for Chemical Industry in Basel, *Swiss Pat.* 92297; *A.*, i, 156.
[79] Ch. Gränacher and A. Mahal, *Helv. Chim. Acta*, 1923, **6**, 467; *A.*, i, 713.
[80] E. E. Turner and F. W. Bury, *T.*, 1923, **123**, 2489.
[81] Chemische Fabriken vorm. Weiler-ter Meer, D.R.-P. 357755; *A.*, i, 114.
[82] D. D. Pratt and R. Robinson, *T.*, 1923, **123**, 739.



Baicalin, a colouring matter present in the roots of *Scutellaria baicalensis*, is converted by hydrolysis into glycuronic acid and baicalein, which appears to be identical with synthetic 5 : 6 : 7-trihydroxyflavone (II).[83]

The Pyrimidines.

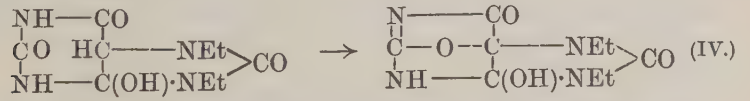
The loose combination between the alloxan and dialuric acid components of alloxantin is illustrated by its decomposition on treatment with diazomethane into products to which formulæ (I) and (II) are assigned. These are also formed when alloxan and dialuric acid or their di-*N*-methyl derivatives are separately treated with diazomethane. The formula (III) for alloxantin is considered to be a better expression of such results than the older ones.



It should be noted that compounds analogous to (I) are obtained by the action of diazomethane on phenanthraquinone, benzil, and other α-diketones.[84]

A number of syntheses of purine derivatives based on Traube's well-known procedure has been published, together with certain improvements in detail.[85]

The oxidation of 4-hydroxy-7 : 9-diethyl-4 : 5-dihydrouric acid by means of ferric chloride, and other mild reagents, yields a product, to which the formula (IV) is assigned.[86]



[83] K. Shibata, S. Iwata, and M. Nakamura, *Acta Phytochim.*, 1923, **1**, 105; *A.*, i, 591; G. Bargellini, *Gazzetta*, 1919, **49**, ii, 47; *A.*, 1919, i, 545.

[84] H. Biltz and H. Paetzold, *Annalen*, 1923, **433**, 64; *A.*, i, 1233.

[85] W. Traube, *ibid.*, **432**, 266; *A.*, i, 1135.

[86] H. Biltz and R. Lemberg, *ibid.*, p. 177; *A.*, i, 957.

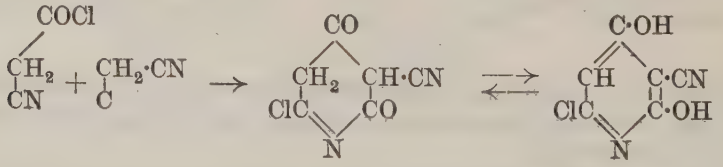
However satisfactory this may be from some points of view, it would appear to be open to serious objection on stereochemical grounds.

The Pyridine Group.

The sodamide method of preparing 2-aminoquinolines has been applied to the preparation of 1-amino*iso*quinoline, and also of 2-aminonicotine, 2 : 6-diaminopyridine, and 6-amino-2-methylpyridine. Nitration of such aminopyridines occurs principally in the 5-, but also in the 3-position, whilst sulphonation and bromination take place in the 5-position. Hydroxy- and halogen derivatives may be prepared from the amines by diazotisation, whilst secondary amines result from heating their hydrochlorides.[87]

2-Hydroxypyridine is produced when pyridine vapour is passed over potassium hydroxide at 320°, whilst an 80 per cent. yield of 2-hydroxyquinoline is similarly obtained at 225°. In this reaction also, the 2-position is exclusively attacked, so that 2-methylquinoline is recovered unchanged after similar treatment.[88]

The condensation of saturated aliphatic aldehydes with ammonia gives rise to a number of pyridine derivatives. Thus from acetaldehyde 2- and 4-picolines, 2-methyl-5-ethyl-, 4-methyl-3-ethyl-, and 2 : 3 : 6-trimethyl-pyridines have been obtained.[89] The chief product of the decomposition of cyanoacetyl chloride, which occurs slowly even at the ordinary temperature, is 6-chloro-2 : 4-dihydroxynicotinonitrile :[90]



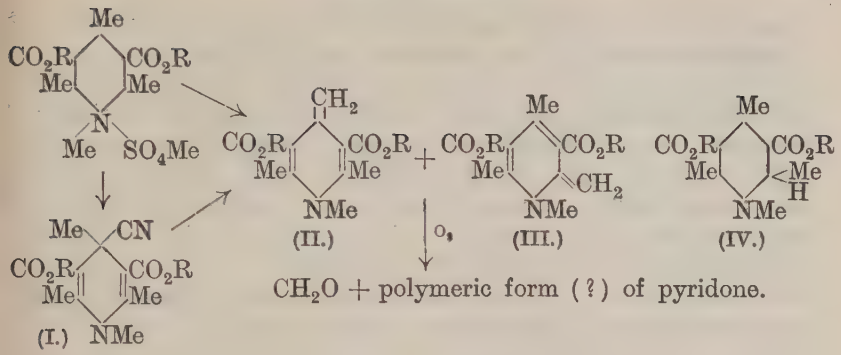
The first representative of the pyridine methides has been prepared by treatment of pyridine methosulphate with sodium hydroxide and is also obtained by decomposition (which occurs slowly even at the ordinary temperature) of the cyano-derivative (1) :

[87] A. E. Tschitschibabin and others, *J. Russ. Phys. Chem. Soc.*, 1921, **50**, 471, 483, 492, 495, 497, 502, 512, 519, 522, 534, 543, 548; *A.*, i, 594—600, 604, 613; J. P. Wibaut and (Miss) E. Dingemanse, *Rec. trav. chim.*, 1923, **42**, 240; *A.*, i, 486.

[88] A. E. Tschitschibabin, *Ber.*, 1923, **56**, [*B*], 1879; *A.*, i, 1121.

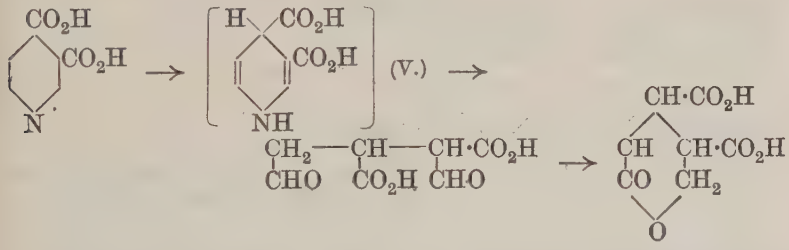
[89] A. E. Tschitschibabin and others, *J. Russ. Phys. Chem. Soc.*, 1923, **54**, 402, 411, 413, 420, 428; *A.*, i, 1121, 1122, 1123; compare *Ann. Reports*, 1906, **3**, 168.

[90] G. Schroeter and Chr. Seidler, *J. pr. Chem.*, 1922, [ii], **105**, 165; *A.*, **i**, 1124.

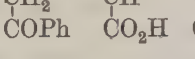


The methide occurs in two interconvertible modifications, respectively reddish-yellow and yellow, and corresponding possibly to the two formulæ (II) and (III). By catalytic reduction, a dihydro-derivative results, which differs from the known compound derived from (II), and hence is assumed to be (IV). Atmospheric oxidation furnishes a black compound of uncertain constitution, which may be a polymeride of the expected pyridone, but is not obtainable from it.[91]

The elimination of ammonia from pyridinecarboxylic acids by reduction with sodium amalgam in warm alkaline solution probably depends on the formation of a dialdehyde, which then undergoes a Cannizzaro rearrangement. For example, in the case of cinchomeronic acid, the change may be represented :



It will be noticed that (V) contains a grouping somewhat similar to that in pyrrole, which latter is easily converted into the oxime of succinaldehyde. Further, 6-phenyl-2-methylcinchomeronic acid has been shown to furnish the acid (I).[92]

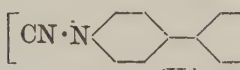


[91] O. Mumm and G. Hingst, *Ber.*, 1923, **56**, [*B*], 2301; *A.*, 1924, i, 83.

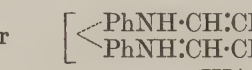
[92] O. Mumm and K. Brodersen, *Ber.*, 1923, **56**, [*B*], 2295; *A.*, 1924, i, 82; compare H. Weidel and J. Hoff, *Monatsh.*, 1892, **13**, 578; *A.*, 1893, i, 114.

Against the view that apophyllenic acid is a 4- rather than a 3-betaine derivative of cinchomeronic acid,[93] it has been urged that a comparison with the behaviour of 2 : 6-dimethylcinchomeronic acid is inadmissible, since in this the 3-carboxyl group is sterically protected. The methiodide of 3-methyl 4-ethyl cinchomeronate yields a mixture of 3- and 4-betaines, in which the former preponderates in spite of the very much easier alkaline hydrolysis of the 4-ester group. It is therefore maintained that betaine formation from the free acid will occur in the 3-position.[94]

The interaction of 4 : 4′-dipyridyl with cyanogen bromide has been investigated. This reagent is known readily to open the pyridine ring,[95] but for the first time in the present instance a primary additive product (II) has been obtained. By treatment of dipyridyl with two molecular proportions of cyanogen bromide and excess of aniline, the normal dianilidodianil dihydrobromide (III) is obtained.[96]

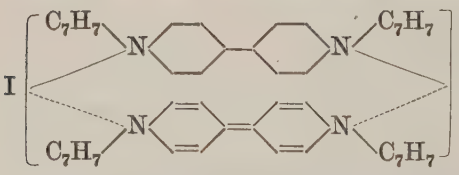


(II.)



(III.)

In confirmation of the views previously expressed on the constitution of the coloured quinhydrones obtained from the reduction of various pyridine derivatives,[97] tetrabenzyldipyridylviolet iodide (I) is converted in acetic acid solution by absorption of atmospheric oxygen into the corresponding dipyridyldibenzyl salt:



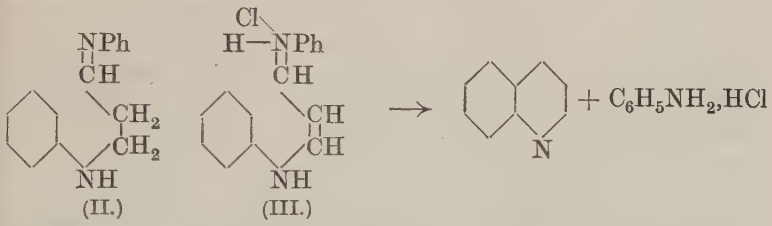
(I.)

Attempts to prepare mixed salts of the type (I) from, for example, dibenzyltetrahydrodipyridyl and dilutidyldiiodobenzylate have failed, tetrabenzyldilutidylviolet iodide being formed in the instance cited.[98]

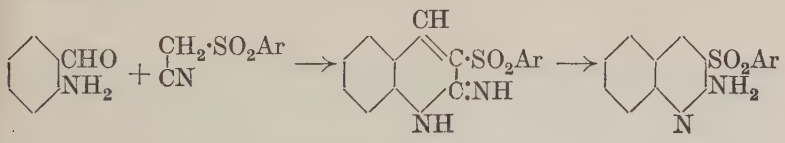
[93] Compare *Ann. Reports*, 1922, **19**, 147.
[94] A. Kirpal and E. Reiter, *Annalen*, 1923, **433**, 112; *A.*, i, 1225.
[95] Compare *Ann. Reports*, 1905, **2**, 149.
[96] W. König (with G. Ebert and K. Centner), *Ber.*, 1923, **56**, [*B*], 751; *A.*, i, 383.
[97] Compare *Ann. Reports*, 1922, **19**, 150.
[98] B. Emmert and O. Varenkamp, *Ber.*, 1923, **56**, [*B*], 491; *A.*, i, 383.

The Quinoline Group.

It has been previously supposed that the Skraup and Doebner and Miller syntheses depend in the first place on the addition of the aromatic amine to the double bond of an unsaturated aldehyde. The behaviour of the ketoanils previously discussed [99] would suggest that this is not quite correct, but that it is rather the anil (for example II) of such an intermediate product from which the quinoline ring is formed. Further evidence in favour of this view is supplied by the easy conversion of the anil of β-anilinoacraldehyde (III) into quinoline when its hydrochloride is heated with zinc chloride : [1]



The formation of quinolines by condensation of *o*-aminobenzaldehyde with bromoacetophenone, acetonylphthalimide, or phenacylphthalimide,[2] or diphenylsulphonylacetone [3] is an obvious special form of the Friedlaender synthesis. More interesting, as involving an imino-condensation, is the reaction represented as follows : [4]



The amino-group in the product is not diazotisable, but may be replaced by hydroxyl.

An extended study [5] of the catalytic reduction of quinoline derivatives has shown that, whilst 6-, 7-, and 8-methylquinolines, like quinoline itself, suffer reduction of the pyridine ring exclusively,

[99] See p. 127.

[1] W. König, *Ber.*, 1923, **56**, [*B*], 1853; *A.*, i, 1127.

[2] G. Bargellini and S. Berlingozzi, *Gazzetta*, 1923, **53**, i, 3; *A.*, i, 482; S. Berlingozzi, *Atti R. Accad. Lincei*, 1923, [v], **32**, i, 339; *A.*, i, 847.

[3] J. Tröger and P. Köppen-Kastrop, *J. pr. Chem.*, 1922, [ii], **104**, 335; *A.*, i, 368.

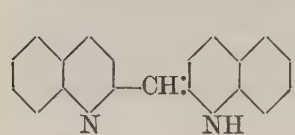
[4] J. Tröger and K. v. Seelen, *ibid.*, **105**, 208; *A.*, i, 1127.

[5] J. v. Braun, W. Gmelin, and A. Schultheiss, *Ber.*, 1923, **56**, [*B*], 1338; **A., i, 835.**

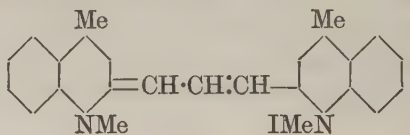
substitution of this ring, as illustrated by the cases of 2-(4)-, 3-(33)-, and 4-(33)-methyl-, of 2 : 3-(44)- and 2 : 4-(80)-dimethyl-, and 2 : 3 : 4-(80)-trimethyl-quinolines, renders it more resistant, so that to a certain extent (indicated by the bracketed figures of percentages) *Bz*-tetrahydro-derivatives are produced. As would be expected, tetrahydroacridine (49) and 2 : 3-trimethylenequinoline (48) exhibit a similar behaviour.[6] It seems to have escaped the investigators concerned that these results are in noteworthy contrast with the fact that, so far as the point has been examined, substitution in the pyridine nucleus renders this more susceptible to attack by oxidation, especially in acid solution.[7]

ω-Trichloro- and ω-tribromo-derivatives are readily prepared from quinaldine by addition of halogen to the base in glacial acetic acid solution, and subsequently boiling the mixture for a few minutes.[8] This is not surprising when it is remembered that the hydrogen atoms concerned are "positive," like those in ethyl malonate and similar easily halogenated compounds.

The interesting suggestion[9] has been made that the coloured forms of salts of di- and tri-quinolylmethanes are not truly quinonoid, as represented, for example, by (I), but rather that they contain a hydrogen atom which is simultaneously within the spheres of



(I.)



(II.)

influence of the two nitrogen and the central carbon atoms, because the absorption spectrum of the compound (I) does not agree with that of the *N*-methyl derivative, but rather with that of *ψ-iso*cyanine iodide. Other reasons advanced seem less forceful. For example, the reactivity of both the methyl groups in (II) is easily explained by the known tautomerism of the *iso*cyanines, and is not a sufficient reason for supposing that a formula with two pyridine nuclei is preferable—although workers on tautomerism may very possibly prefer this reason on other grounds. Similarly, the formation of *iso*nitro- and oximino-derivatives by direct action of nitric and nitrous acids respectively can be met by the quinonoid formula.

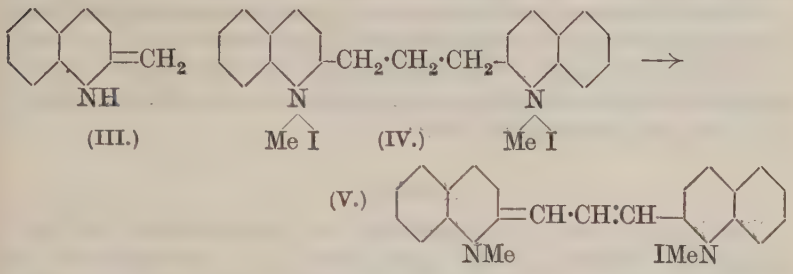
[6] J. v. Braun, A. Petzold, and A. Schultheiss, *Ber.*, 1923, **56**, [*B*], 1347; *A.*, i, 836.

[7] Compare, for example, W. v. Miller, *Ber.*, 1891, **24**, 1900; *A.*, 1891, 1094.

[8] D. L. Hammick, *T.*, 1923, **123**, 2882.

[9] G. Scheibe, *Ber.*, 1923, **56**, [*B*], 137; *A.*, i, 250.

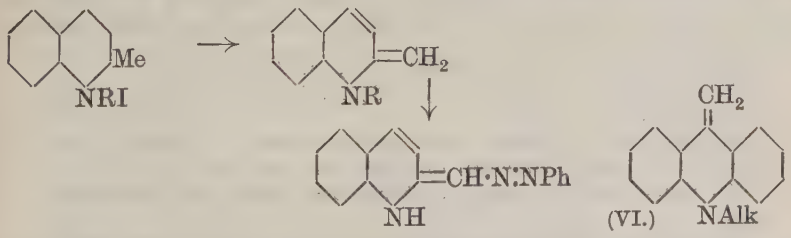
As mentioned in last year's Report,[10] the methylene derivative (III) had previously been suggested as a possible intermediary in the typical condensations of 2-methylquinolines. At the same time, it was recognised that such a methylene derivative might be



more easily formed from quaternary ammonium salts, and hence provide an explanation of their superior reactivity. An illustration of this is supplied in the condensation of quinaldine methiodide with formaldehyde in hot alcoholic solution to the derivative (IV), previously suggested as the intermediate product in the formation of dimethylcarbocyanine (V). Its conversion into the latter was actually achieved by treatment with hot alcoholic sodium hydroxide, but the yield was increased tenfold by the presence of a quaternary ammonium salt. The importance of the latter in the usual preparation of the dyestuff is already known, but its function is not clear, since in the experiments under consideration the composition of the product is independent of the nature of the salt used.[11]

The corrected formula for cryptocyanine [12] has been justified, and in the same paper a new general method of preparing carbocyanines and *iso*cyanines is described.[13]

The formation of methylene derivatives has also been assumed to explain the interesting dealkylation which occurs when quinaldinium alkyliodides are treated simultaneously with a molecular proportion each of sodium hydroxide and aryldiazonium chloride :



In support of this view, vinyldimethylamine is also known to

[10] See p. 156.
[11] Miss F. M. Hamer, *T.*, 1923, **123**, 246.
[12] *Ann. Reports*, 1921, **18**, 139.
[13] W. H. Mills and W. T. K. Braunholtz, *T.*, 1923, **123**, 2804.

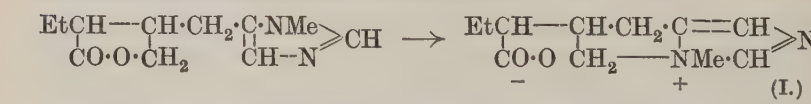
couple,[14] and it has been found possible to isolate (VI). Somewhat curiously, however, the investigation is not rounded off by showing that the last compound couples, or whether coupling with vinyldimethylamine involves dealkylation.[15]

An examination of the syntheses of tetrahydro*iso*quinoline from phenylethylamine and formaldehyde [16] has shown that the small quantity of the desired base produced is accompanied by a considerable amount of unchanged material and a notable amount of di-β-phenylethylaminomethane.[17]

Alkaloids.

The lactonic nature of pilocarpine and *iso*pilocarpine has been confirmed. Further, it has been shown that isomerisation of pilocarpine occurs under the influence of traces of sodium ethoxide, proceeds more rapidly than delactonisation, does not occur in aqueous solution, and is not applicable to the salts resulting from delactonisation by alkali. The lactonic grouping is therefore essential to the change, which seems comparable with that of hyoscyamine to atropine, and therefore is considered most probably to consist in partial racemisation of one of the two asymmetric carbon atoms of the lactonic group.[18]

*meta*Pilocarpine, which is produced when pilocarpine hydrochloride is heated for a longer time and at a higher temperature than is necessary for the preparation of *iso*pilocarpine hydrochloride, is found to differ from its generators in being optically inactive, and an extremely weak base, but very soluble in water. The compound is therefore considered to be a betaine (I).[19]



(I.)

The constitution of ricinine has been finally determined by replacing its reactive 4-methoxyl group successively by chlorine and hydrogen. The product, ricinidine, on the basis of the earlier

[14] K. H. Meyer, *Ber.*, 1921, **54**, [*B*], 2277; *A.*, 1921, i, 851.

[15] W. König, *ibid.*, 1923, **56**, [*B*], 1543; *A.*, i, 862; A. Adam, *Wissensch. Ind.*, 1923, **2**, 2; *A.*, i, 1129.

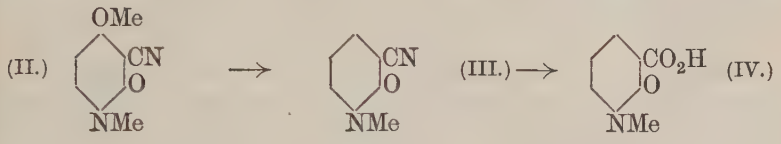
[16] A. Pictet and T. Spengler, *Ber.*, 1911, **44**, 2036; *A.*, 1911, i, 750; H. Decker and P. Becker, *Annalen*, 1913, **395**, 342; *A.*, 1913, i, 291.

[17] H. Kondo and E. Ochiai, *J. Pharm. Soc. Japan*, 1923, **495**, 313; *A.*, i, 837.

[18] M. and M. Polonovski, *Bull. Soc. chim.*, 1922, [iv], **31**, 1185, 1201; *A.*, 1923, i, 129, 130. Readers of these papers will note that in the formulæ employed, the side chain is erroneously attached in the 4- instead of in the 5-position; compare F. L. Pyman, *T.*, 1910, **97**, 1819.

[19] *Ibid.*, p. 134; *A.*, 1923, i, 130.

formulæ,[20] might have been expected to furnish on treatment with caustic alkali either 2-pyridonyl-1-acetic acid or 1-methyl-2-pyridone-6-carboxylic acid. Actually, however, 1-methyl-2-pyridone-3-carboxylic acid (IV) was obtained, identical with the product of the action of methyl iodide on the disilver salt of 2-hydroxypyridine-3-carboxylic acid. It therefore follows that ricinidine is the corresponding nitrile (III), and that ricinine is 3-cyano-4-methoxy-1-methyl-2-pyridone (II) : [21]



This conclusion has been confirmed by synthesis. 4-Chloroquinolinic acid, from the oxidation of 4-chloroquinoline, was converted through its imide into 4-chloro-2-aminoquinoline-3-carboxylic acid, from which the 2-hydroxy-derivative was prepared and converted into 2 : 4-dichloro-3-cyanopyridine. The 2 : 4-dimethoxy-derivative obtained from this was converted by treatment with methyl iodide into a product identical with natural ricinine.[22] It has been shown by exactly analogous methods, both analytical and synthetic, that echinopsine is 1-methyl-4-quinolone.[23]

Thus ricinine, echinopsine, and cytisine are pyridones, but strychnine is probably not, because it does not show the colour reactions which characterise these compounds.[24]

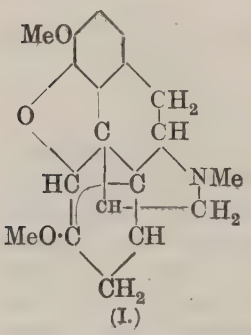
The inference that the base scopoline, isolated as a product of the acid hydrolysis of scopolamine, is not the base of which the alkaloid is the tropyl derivative [25] has been confirmed by the preparation of the latter base, scopine, by hydrolysis with pancreatic lipase in ammonia–ammonium chloride buffer solution. As would be expected, scopine is readily converted into scopoline by heat or treatment with alkali or acid. It is more stable towards acid than towards alkali.[26]

Aldehydes have been prepared from quinine and cinchonine

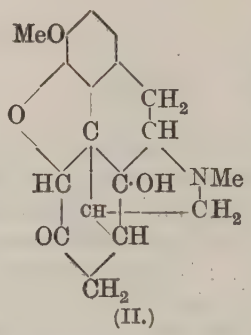
[20] Compare *Ann. Reports*, 1922, **19**, 157.
[21] E. Späth and G. Koller, *Ber.*, 1923, **56**, [*B*], 880; *A.*, i, 594.
[22] *Ibid.*, p. 2454.
[23] E. Späth and A. Kolbe, *Monatsh.*, 1923, **43**, 469; *A.*, i, 479; compare M. Greshoff, *Rec. trav. chim.*, 1900, **19**, 360; *A.*, 1900, i, 338.
[24] E. Späth and G. Koller, *loc. cit.*
[25] Compare *Ann. Reports*, 1922, **19**, 160.
[26] R. Willstätter and E. Berner, *Ber.*, 1923, **56**, [*B*], 1079; *A.*, i, 701.

and their acetyl and benzoyl derivatives by first converting them into ozonides.[27]

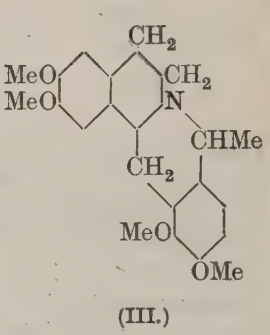
Reference has already been made (p. 127) to the reason for adopting a fundamental modification of the formulæ assigned to the morphine alkaloids. The formula (I) is adopted for thebaine to explain its hydrolysis to codeinone, and its oxidation by acid hydrogen peroxide to hydroxycodeinone, of which the formula is most probably (II), since the ketone furnishes no osazone and, unlike β-hydroxyketones, shows no tendency to lose the elements of water.[28]



(I.)



(II.)



(III.)

As a preliminary to the further confirmation of these formulæ, the molecular structures of codeinone, thebainol, and thebainone have been shown respectively to contain the groupings ·CH_2·CO·, ·CH_2·CO·CH_2·, and ·CH:CH·CO·CH_2·.[29]

Both anhalonidine and pellotine [30] have been synthesised by the usual methods from ethyl 5-acetoxy-3 : 4-dimethoxyphenylethylaminoacetate.[31]

The application to corydaline of the Hofmann and the Emde methods of degradation by exhaustive methylation has shown the latter to be the more trustworthy in this instance. For whereas, as would be expected, trimethylamine was obtained in the latter case only after the third treatment, in the former it was produced, although in poor yield, after the second. This is attributed to possible slight splitting up of the corydaline methiodide into base and methyl iodide during the heating with sodium hydroxide. The methyl iodide could then combine with the base obtained by the degradation proper and give a methiodide, which immediately in turn would be decomposed and yield trimethylamine.[32]

[27] L. Seekles, *Rec. trav. chim.*, 1923, **42**, 69; *A.*, i, 237.
[28] J. M. Gulland and R. Robinson, *T.*, 1923, **123**, 980.
[29] *Idem, ibid.*, p. 998.
[30] Compare *Ann. Reports*, 1922, **18**, 162.
[31] E. Späth, *Monatsh.*, 1923, **43**, 477; *A.*, i, 479.
[32] E. Späth and E. Mosettig, *Annalen*, 1923, **433**, 138; *A.*, 1924, i, 74.

In connexion with the question of the constitution of corydaline,[33] the base (III) has been synthesised, but found not to be identical with the racemic form of the alkaloid.[34]

A preparation of the alkaloids from *Corydalis cava*, in which an unusually small amount of corydaline was present, was found to contain, besides the alkaloids previously observed, *d*-tetrahydropalmatine and a base, corypalmine, differing from the latter in containing a free hydroxyl in place of the methoxyl group. At the same time, the existence of a similar relationship between corybulbine and corydaline[35] was confirmed by conversion of the former into the latter by methylation.[36]

The investigation[37] of the alkaloids of the Calabar bean appears to be entering a stage at which it may be convenient to summarise the present position. One constituent, eserine (or physostigmine), is a lævorotatory, strongly alkaline compound, easily convertible into a dihydro-derivative. It is hydrolysed by sodium ethoxide in absolute alcoholic solution to methylurethane and eseroline, and may be regenerated from the latter by treatment with methylcarbimide at the ordinary temperature, although at 100° the product is *iso*eserine. Eseroline contains two methylimino-groups[38] and a phenolic hydroxyl group etherifiable by means of ethyl *p*-toluenesulphonate. The ether so prepared, eserethole, when converted into its methiodide and treated with sodium hydroxide furnishes, in place of the expected methine, by a reaction apparently akin to the conversion of quinolinium salts into quinolanols, a compound, esoline, containing the elements of an extra molecule of water. From the last compound, two distinct methiodides (only one of which suffers degradation on treatment with alkali) are obtainable, as well as a dimethiodide. Correspondingly, if the methiodide be treated with excess of methyl iodide and sodium ethoxide, an ethoxy-derivative is obtained, which is converted into esoline when its aqueous suspension is boiled. Correspondingly, it has been independently observed that when eserethole is

[33] Compare *Ann. Reports*, 1922, **18**, 163.

[34] E. Späth and E. Mosettig, *loc. cit.*

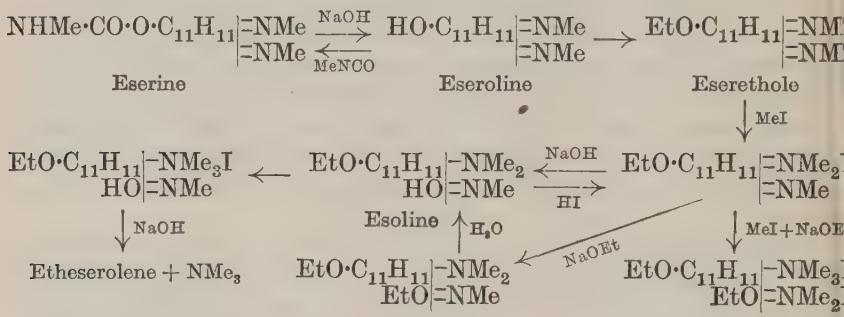
[35] Compare J. Dobbie, A. Lauder, and P. Paliatseas, *T.*, 1901, **79**, 89; J. Gadamer and D. Bruns, *Arch. Pharm.*, 1903, **241**, 634; *A.*, 1904, i, 185.

[36] E. Späth, E. Mosettig, and O. Tröthandl, *Ber.*, 1923, **56**, [*B*], 875; *A.*, i, 593.

[37] M. Polonovski and others, *Bull. Soc. chim.*, 1915, [iv], **17**, 235, 244; 1916, **19**, 27; 1918, **23**, 335, 356; *Compt. rend.*, 1923, **176**, 480, 1896; **177**, 127; *A.*, 1915, i, 891, 892; 1916, i, 221; 1918, i, 504, 505; 1923, i, 700, 831, 831; E. Stedman, *T.*, 1921, **119**, 891; G. Barger and E. Stedman, *T.*, 1923, **123**, 758.

[38] J. Herzig and H. Lieb, *Monatsh.*, 1918, **39**, 285; *A.*, 1918, i, 504.

treated with excess of methyl iodide and sodium ethoxide, a dimethiodide is produced. These relationships may be represented as follows : [39]



It would be inappropriate to do more than refer to the tentative suggestions [40] in regard to constitutional formulæ for these compounds until outstanding difficulties have been cleared up. For example, whilst esoline ethyl ether dimethiodide is optically inactive, etheserolene is stated to be lævorotatory.

Geneserine is a congener of eserine, into which it passes on reduction, and furnishes analogous derivatives, geneseroline and geneserethole, which in turn are similarly convertible into eseroline and eserethole.

J. KENNER.

[39] The mode of representing the various compounds has been adopted from the paper by G. Barger and E. Stedman, *loc. cit.*, but modified to exhibit the parallelism between the results of the two sets of investigations.

[40] Straus, *Annalen*, 1913, **401**, 358; M. and M. Polonovski, *Compt. rend.*, 1923, **176**, 1896; *Bull. Soc. chim.*, 1923, [iv], **33**, 970; *A.*, i, 831, 940.

ANALYTICAL CHEMISTRY.

THE volume of work published on analytical chemistry during the past year has exceeded even those of the years preceding the war, and, in order to make a survey of the whole field, it has been necessary to select mainly those methods in which a new principle has been devised or the scope of an old one extended, and to omit references to modifications which are of more limited application.

Physical Methods.

Apart from electro-chemistry, which is dealt with in a separate section, the main advance in this branch of the subject has been in the extension of various optical methods to analysis.

The refractive indices of selenious and selenic acids in aqueous solution have been determined for various concentrations, and it has been shown that a determination of this constant affords an accurate means of estimating the two acids.[1]

The various factors influencing the accuracy of the analysis of mixtures of organic liquids by means of the water interferometer have been investigated and precautions to eliminate these and render the method trustworthy have been devised.[2]

A modified form of the Kleinmann nephelometer has been described, in which the drawbacks pointed out by Weinberg[3] have been avoided. The instrument can be used for the estimation of small amounts of calcium in blood, etc., with a fair degree of accuracy.[4] It is also useful for estimating minute quantities of protein.[5]

The oxy-acetylene flame has been adapted to the spectral analysis of minerals, and although the method is not so generally applicable as the spark spectrum, it gives good results with the alkali and alkaline-earth metals, and with many heavy metals, but is less satisfactory with magnesium, zinc, cadmium, and mercury.[6]

A method of quantitative spectroscopic analysis has been based on the observation of the most sensitive rays (raies ultimes) of an

[1] H. W. Stone, *J. Amer. Chem. Soc.*, 1923, **45**, 29; *A.*, ii, 178.
[2] E. Cohen and H. R. Bruins, *Z. physiol. Chem.*, 1923, **103**, 337; *A.*, ii, 188.
[3] A. A. Weinberg, *Biochem. Z.*, 1921, **125**, 292; *A.*, 1922, ii, 309.
[4] H. Kleinmann, *ibid.*, 1923, **137**, 144; *A.*, ii, 429.
[5] P. Rona and H. Kleinmann, *ibid.*, 1923, **140**, 461; *A.*, ii, 890.
[6] A. de Gramont, *Compt. rend.*, 1923, **176**, 1104; *A.*, ii, 429.

element, and comparison, by means of photography, of the spectrum of an unknown substance with those of standard specimens of salts and alloys.[7]

Errors of measurement of the mean wave-lengths of absorption bands, due to the indefiniteness of the edges, are eliminated in a coincidence method of measurement, in which the spectroscope is so constructed that the spectra are seen side by side, but reversed in direction. Then by setting one edge of a band so that it coincides with the same edge of the one above, the mean wave-length can be read on the micrometer scale with a limit of error of about 0·6 Å.U.[8]

The basis of a new method of measuring the colour of brown solutions, such as tannin extracts, is that of measuring the depth of the liquid at which a half, or other fraction, of the light is absorbed at three or four parts of the spectrum. Colour screens, which may be calibrated by comparison with standard flames, are used, and a solution of iron ammonium sulphate forms the colour standard to which the measurements made with the colour screens are referred.[9]

Reference may also be made to a spectrophotometric method of identifying different dyes by quantitative measurements of their intensity of absorption under varied conditions.[10]

A new polarimetric method of estimating basic groups in different types of compounds consists in determining the effect of the basic substance upon the velocity of the inversion of sucrose by hydrochloric acid. For this purpose the relationship between the velocity coefficient of inversion, k, and the normality, N, of the acid is first established over a wide range and expressed as an equation, in which the value of the constants is then ascertained.[11]

For the polarimetric estimation of malic and tartaric acids advantage has again been taken of the fact that uranium and molybdenum compounds cause an increase in the optical activity of organic substances, and the relationship between the concentration of solutions of the acids and their optical activity has been determined under specified conditions.[12]

There have been few contributions to the subject of viscometry, but mention may be made of an apparatus by means of which

[7] W. F. Meggers, C. G. Kiess, and F. J. Stimson, *Bull. Bur. Standards*, 1922, **18**, 235, *Sci. Paper* No. 444; *A.*, ii, 81.

[8] H. Hartridge, *Proc. Roy. Soc.*, 1923, [*A*], **102**, 575; *A.*, ii, 105.

[9] H. R. Procter, *J. Soc. Chem. Ind.*, 1923, **42**, 73; *A.*, ii, 270.

[10] W. C. Holmes, *Ind. Eng. Chem.*, 1923, **15**, 833; *A.*, ii, 332.

[11] J. Groot, *Biochem. Z.*, 1923, **137**, 517; *A.*, ii, 503.

[12] F. Auerbach and D. Krüger, *Z. Unters. Nahr. Genussm.*, 1923, **46**, 97; *A.*, ii, 884.

the viscosity and surface tension of a liquid at high temperatures may be successively measured.[13]

Gas Analysis.

Traces of nitrogen in hydrogen may conveniently be estimated by a modification of the ordinary method of combustion over copper oxide and measurement of the residual gas.[14]

The use of phosphorus as an absorbent for oxygen in gas analysis obviates some of the drawbacks of alkaline pyrogallol, but its absorbent action is not so rapid.[15]

Various modifications of the method of estimating carbon monoxide in air by absorption with defibrinated blood have been studied, and an apparatus for the purpose has been devised.[16] The tannin reaction of Weltz with the blood which has absorbed the carbon monoxide from the air has been developed into a quantitative method,[17] and permanent standards for the purpose have been prepared. It is shown that the accuracy of the method is within the limits of 0·005 to 0·03 per cent. of the total volume of carbon monoxide in the air tested.[18]

When estimating methane in mine gases by combustion in contact with a glowing platinum spiral, complete oxidation is not attained unless the platinum is brought to a white heat and the methane exposed to its action for three to four minutes.[19]

Sulphuric acid of 87 per cent. strength has been found a suitable reagent for separating propylene from ethylene. All the propylene (when not present in too large excess) is absorbed within ten minutes, but scarcely any of the ethylene.[20]

For the analysis of gas mixtures containing methyl chloride and other compounds soluble in organic solvents, the gas is burned with a measured excess of oxygen in a combustion pipette over potassium hydroxide solution, and the absorbed chloride estimated. Measurement of the oxygen consumed affords a check on the result.[21]

[13] F. V. von Hahn, *Chem. Ztg.*, 1923, **47**, 402; *A.*, ii, 379.
[14] R. L. Dodge, *J. Amer. Chem. Soc.*, 1923, **43**, 1688; *A.*, ii, 653.
[15] A. Holmes, *Ind. Eng. Chem.*, 1923, **15**, 357; *A.*, ii, 332.
[16] M. Nicloux, *Bull. Soc. chim.*, 1923, [iv], **33**, 818; *A.*, ii, 578.
[17] V. Andriska, *Z. Unters. Nahr. Genussm.*, 1923, **46**, 43; *A.*, ii, 876.
[18] R. R. Sayers, W. P. Yant, and G. W. Jones, *U.S. Bur. Mines Rept. Investigations*, 1923, No. 2486; *A.*, ii, 789.
[19] J. W. Whitaker, *Fuel*, 1923, **2**, 201; *A.*, ii, 586.
[20] H. Tropsch and A. P. Philippovich, *Brennstoff-Chem.*, 1923, **4**, 147; *A.*, ii, 509.
[21] R. H. McKee and S. P. Burke, *Ind. Eng. Chem.*, 1923, **15**, 578; *A.*, ii, 586.

Investigation of the rate of absorption of gaseous oxides of nitrogen has shown that those corresponding approximately with the formula N_2O_3 are absorbed much more rapidly than nitrogen dioxide or peroxide. Absorption with sulphuric acid is preferable to absorption with alkaline liquids for nitrous gases, since less nitrogen in the higher state of oxidation is obtained. In the case of the alkaline absorbents, secondary reactions with water or water vapour occur.[22]

A liquid secondary amine, such as ethylaniline, is used as an absorbent for nitrous anhydride in a method of estimating nitric oxide by combustion with oxygen. The excess of oxygen is then absorbed by means of alkaline pyrogallol, and the volume of nitric oxide obtained from the contraction of volume.[23]

Among new forms of apparatus described, mention may be made of a modification of the Hempel explosion pipette, in which leakage of gas during the explosion is prevented,[24] and of a burette with two parallel limbs connected by means of a capillary tube.[25]

Agricultural Analysis.

The method of estimating carbon by oxidation with sulphuric acid and silver dichromate [26] has been adapted to soils, and is shown to yield results in agreement with those obtained by the cupric oxide method.[27] From a comparison of this sulpho-chromic method with the standard method of igniting the soil and weighing the carbon dioxide formed, the conclusion is drawn that either method may be used for estimating humus. An approximate idea of the amount of humus may be obtained from an estimation of the chlorine in a soil.[28]

Another method of estimating soil humus has been based upon its extraction by means of aqueous pyridine. Combined humus is subsequently estimated by extracting the residual soil, with the same solvent, after treatment with dilute hydrochloric acid.[29]

A microscopical examination, with an eye-piece micrometer, of the fractions of soil separated from the clay by the usual mechanical treatment enables an estimation of the relative proportions of

[22] A. Sanfourche, *Bull. Soc. chim.*, 1922, [iv], **31**, 1248; *A.*, ii, 84.
[23] A. Koehler and M. Marqueyrol, *Mém. Poudres*, 1922, **19**, 359; *A.*, ii, 178.
[24] K. Tiddy, *Gas World*, 1923, **79**, 187; *A.*, ii, 694.
[25] H. J. M. Creighton, *Trans. Nova Scotia Inst. Sci.*, 1919—20, **15**, [2], 115; *A.*, ii, 780.
[26] Compare *Ann. Reports*, 1922, **19**, 172.
[27] L. J. Simon, *Compt. rend.*, 1923, **176**, 1409; *A.*, ii, 506.
[28] V. Agafonoff, *ibid.*, pp. 177, 404; *A.*, ii, 668.
[29] M. Piettre, *ibid.*, p. 1329; *A.*, i, 736.

mineral particles and colloidal aggregates to be made by direct observation.[30]

For the colorimetric estimation of the hydrogen-ion concentration in soils, a clear solution may be readily obtained by the use of Parker's method of downward displacement.[31] The results obtained by titrating the extract, with the use of brom-cresol purple as indicator, agree closely with electrometric estimations.[32]

An apparatus for measuring the oxygen-supplying power of soil consists essentially of a closed porous pot connected with a bottle containing alkaline pyrogallol. The pot is buried in soil under standardised conditions, and the rate of oxygen-diffusion is indicated by the time required for the oxygen to diffuse through the walls of the pot and change the colour of the indicator to a standard colour.[33]

Mention may also be made of a new form of respirometer designed to afford an accurate measurement of the oxygen consumed and carbon dioxide produced by seeds, etc., from a total volume of air in a given time.[34]

Low and irregular results may be obtained in estimating small amounts of nitrates in soils by the phenoldisulphonic acid method, owing to retention of nitrate by filter paper. This may be prevented by the use of a particular type of coarse filter-paper.[35]

The results obtained in estimating potassium and "citric-soluble" phosphoric acid in soils and fertilisers vary considerably with the fineness of the material, but are not appreciably affected by ignition of the soil extract. Variations in the duration of shaking or the volume of citric acid solution do not have much influence on the phosphoric acid results.[36]

Organic Analysis.

Qualitative.—The use of perchloric acid as a general reagent enables many amines and alkaloids to be classed into two large groups, which can be distinguished by the form and optical properties of the microcrystalline precipitates.[37] Potassium ferro-

[30] W. H. Fry, *J. Agric. Res.*, 1923, **24**, 879; *A.*, ii, 892.
[31] F. W. Parker, *Science*, 1921, **54**, 438; *A.*, 1922, i, 511.
[32] C. T. Gimingham, *J. Agric. Sci.*, 1923, **13**, 69; *A.*, ii, 668.
[33] L. M. Hutchins and B. E. Livingstone, *J. Agric. Res.*, 1923, **25**, 133; *A.*, i, 1166.
[34] G. T. Harrington and W. Crocker, *ibid.*, p. 101; *A.*, i, 424.
[35] C. T. Gimingham and R. H. Carter, *J. Agric. Sci.*, 1923, **13**, 60; *A.*, ii, 577.
[36] H. F. L. Bischoff and B. de C. Marchand, *J. S. African Chem. Inst.*, 1923, **6**, 53; *A.*, ii, 786.
[37] V. Cordier, *Monatsh.*, 1923, **43**, 525; *A.*, ii, 347.

cyanide is another group reagent for many of the common alkaloids, which combine with it to form crystalline compounds of distinctive form.[38]

A study of Schiff's rosaniline and sulphurous acid reaction for aldehydes has shown that the violet coloration is only trustworthy as a test when the solution has a certain acidity. In the case of a number of organic compounds which do not contain aldehydic groups, a red coloration may appear owing to the liberation of rosaniline.[39]

A new test for aldehydes is based upon the gradual hydrolysis of their compounds with sodium hydrogen sulphite, with liberation of sodium hydroxide, which is indicated by a pink coloration with phenolphthalein. Conversely, formaldehyde in presence of phenolphthalein may be used for the detection of sulphites.[40]

Another general reagent for aldehydes is benzidine, which gives different colorations with different types of aldehydes.[41]

Acraldehyde reacts with phloroglucinol in ethereal solution, in presence of water and hydrochloric acid, to form a red, aqueous solution (or purple precipitate in presence of excess of acraldehyde). Apparently the reaction is due to the same compound which causes the Kreis reaction in rancid fats.[42]

Various colour reactions for the detection of sterols have been described, based on their interaction with sulphuric acid, formaldehyde, and acetic anhydride (or acetic acid), or with acetic anhydride and nitric acid. Sterolins may be differentiated from sterols by the different colorations which they give with thymol in the presence of sulphuric acid. It is suggested that essentially all the colour reactions for sterols in solution are very similar in character.[43]

A violet coloration, resembling that given by liver oils with sulphuric acid,[44] is produced when a solution of cholesterol and furfuraldehyde or ω-hydroxymethylfurfuraldehyde is treated with sulphuric acid. The reaction is capable of detecting 0·1 mg. of cholesterol.[45]

Of the colorations given by certain alkylglycerols (after oxidation with bromine) with certain alkaloids and phenols, only that produced by codeine (blue coloration) [46] will differentiate glycerol from

[38] H. I. Cole, *Philippine J. Sci.*, 1923, **23**, 97; *A.*, ii, 703.
[39] K. Josephson, *Ber.*, 1923, **56**, [*B*], 1771; *A.*, ii, 664.
[40] J. Estalella, *Anal. Fis. Quím.*, 1922, **20**, 271; *A.*, ii, 98.
[41] P. N. van Eck, *Pharm. Weekblad*, 1923, **60**, 1204; *A.*, ii, 887.
[42] W. C. Powick, *Ind. Eng. Chem.*, 1923, **15**, 66; *A.*, ii, 191.
[43] G. S. Whitby, *Biochem. J.*, 1923, **17**, 5; *A.*, ii, 344.
[44] Compare *Ann. Reports*, 1922, **19**, 170.
[45] A. Harden and R. Robison, *Biochem. J.*, 1923, **17**, 115; *A.*, ii, 347.
[46] G. Denigès, *Précis de Chimie analytique*, 1920, 151.

its homologues. None of the oxidation reactions of glycerol with potassium permanganate is specific.[47]

A characteristic reaction for oxalic acid depends upon the fact that it gives a blue or green zone coloration with resorcinol and sulphuric acid, whereas other organic acids give yellow or red colorations.[48]

The so-called pyrrole reaction (red coloration of pine shaving moistened with hydrochloric acid and exposed to pyrrole vapour) has been shown to be due, not to resin, but probably to coniferin. It is given strongly by asparagus, which contains coniferin, but not resin.[49]

Certain phenols give specific colorations with copper. For example, quinol gives a blue coloration, the intensity of which is proportional to the amount of copper, and α-naphthol gives a violet coloration, which serves to distinguish it from β-naphthol.[50]

Various tests for distinguishing between glutin and chondrin have been described, such as the precipitation of the barium salt of chondroitinsulphonic acid, which is optically active ($[\alpha]_D = +46{\cdot}5°$).[51]

Quantitative.—Alumina has been shown to have several advantages over other substances as an absorbent for water in elementary analysis.[52]

A new method of combustion analysis depends upon heating the substance with cupric oxide in an exhausted silica tube, and measuring the products of combustion.[53]

Further applications of the use of silver dichromate and sulphuric acid as an oxidising agent for combustion have been described, in addition to its use for the estimation of humus referred to in another section of this Report.[54]

In estimating carbon and hydrogen in organic compounds containing arsenic and mercury, satisfactory results may be obtained by a modification of Dennstedt's method.[55]

Various new methods of estimating halogens in organic sub-

[47] R. Delaby, *Compt. rend.*, 1923, **176**, 396; *A.*, ii, 264.
[48] Muller, *Bull. Assoc. Chim. Sucr.*, 1922, **40**, 169; *A.*, ii, 346.
[49] E. S. Chotinski, *J. Russ. Phys. Chem. Soc.*, 1917, **49**, 149; *A.*, ii, 444.
[50] J. Aloy and A. Valdiguié, *Bull. Soc. chim.*, 1922, **31**, 1176; *A.*, ii, 91.
[51] M. A. Rakuzin, *Chem. Ztg.*, 1923, **47**, 602; *A.*, ii, 667.
[52] H. L. Fischer, H. L. Faust, and G. H. Walden, *Ind. Eng. Chem.*, 1922, **14**, 1138; *A.*, ii, 83.
[53] L. Hackspill and G. de Heeckeren, *Compt. rend.*, 1923, **177**, 59; *A.*, ii, 578.
[54] A. J. A. Guillaumin, *ibid.*, 1923, **176**, 1065; *A.*, ii, 432.
[55] M. Falkov and G. W. Raiziss, *J. Amer. Chem. Soc.*, 1923, **45**, 998; *A.*, ii, 336.

stances have been published. In the case of certain compounds, hydrazine may be used as a reducing agent, the volume of nitrogen evolved (which depends upon the proportion of halogen) being measured.[56] Combustion in a current of ammonia gas can be used for organic halogen compounds, except those of the aromatic series, for which a mixture of ammonia and hydrogen is required.[57] In the case of certain volatile compounds, chlorine can be estimated by burning the substance in a wickless lamp in a current of hydrogen, igniting the vapours in oxygen, and titrating the halogen in the products of the combustion, after absorption in sodium carbonate.[58] A modification of this method consists in dissolving the substance in benzaldehyde, or a mixture of benzaldehyde and alcohol, and burning the solution in the lamp.[59]

For the gravimetric estimation of organic phosphorus, the substance may be oxidised as in the Kjeldahl process, and the phosphorus precipitated as phosphomolybdate, which is subsequently converted into magnesium ammonium phosphate.[60]

Perkin's method [61] for the estimation of the acetyl group gives better results when an aromatic sulphonic acid is used for the hydrolysis, instead of sulphuric acid.[62]

It has been shown that the nature and position of substituent groups have an accelerating or retarding influence on the reaction of the nitro-groups in Kjeldahl's process, and certain constituent groups can be classified on this basis.[63]

A process of reduction with ferrous sulphate and estimation of the unoxidised iron salt enables aliphatic nitrates to be estimated in the presence of certain aromatic nitro-compounds.[64]

Certain amines with a dissociation constant of not less than 5×10^{-9} may be separated from their (preferably neutral) solution by treatment with "permutite," and the principle has been adapted to the estimation of adrenaline.[65]

Turning to individual organic compounds, it has been shown

[56] A. K. Macbeth, *Chem. News*, 1922, **125**, 305; *A.*, ii, 34.
[57] J. Heslinga, *Diss. Delft*, 1923, 1; *A.*, ii, 782.
[58] J. Voigt, *Z. angew. Chem.*, 1922, **35**, 634; *A.*, ii, 34.
[59] K. Rübke, *ibid.*, 1923, **36**, 136; *A.*, ii, 249.
[60] W. Jones and M. E. Perkins, *J. Biol. Chem.*, 1923, **55**, 343; *A.*, ii, 432.
[61] A. G. Perkin, *T.*, 1905, **87**, 107.
[62] K. Freudenberg, *Annalen*, 1923, **433**, 230; *A.*, ii, 884.
[63] B. M. Margosches and W. Kristen [with E. Scheinost], *Ber.*, 1923, **56**, [*B*], 1943; *A.*, ii, 785.
[64] W. J. Huff and R. D. Leitch, *J. Amer. Chem. Soc.*, 1922, **44**, 2643; *A.*, ii, 36.
[65] J. C. Whitehorn, *J. Biol. Chem.*, 1923, **56**, 751; *A.*, ii, 798.

that formaldehyde cannot be directly estimated by the usual methods in presence of copper.[66]

A useful method of estimating formic acid by titration has been based on the fact that one molecule of hydrogen chloride is liberated in the reduction of mercuric chloride by a formate,[67] and an improved gravimetric method based on the reduction of mercuric to mercurous chloride has been worked out.[68]

An analogous method for abietic acids depends upon the reduction of mercuric acetate and gravimetric estimation of the mercurous acetate.[69]

The naturally-occurring *d*-tartaric acid may be quantitatively precipitated as a calcium or lead salt after the addition of an equivalent quantity of the *l*-acid.[70]

There have not been many contributions to the methods of analysing oils and fats, but mention may be made of a gravimetric method of estimating the hydroxyl and acetyl values,[71] and of the use of pyridine sulphate dibromide for the rapid estimation of the iodine value.[72] A new method of estimating arachidic and lignoceric acids has also been devised; it is based on the relative insolubility of their magnesium salts in 90 per cent. alcohol.[73]

Investigation of the conditions under which gallotannin is precipitated by gelatin has shown that the precipitation is quantitative when the ratio of tannin to gelatin is not less than 2 : 1. There is an optimal hydrogen-ion concentration for the precipitation of each individual tannin.[74]

A colorimetric method of estimating gallotannin and its derivatives has been based upon the apparently specific violet coloration given by the pyrogallic group with a ferrous tartrate reagent. The coloration is compared with that given by a standard solution of pyrogallol or gallic acid. In the case of mixtures of gallotannin and gallic acid, both substances are estimated together in terms of gallic acid, the gallotannin is then precipitated by means of quinine hydrochloride, and the gallic acid in the filtrate estimated as before.[75]

[66] M. Jakeš, *Chem. Ztg.*, 1923, **47**, 386; *A.*, ii, 442.
[67] B. Holmberg and S. Lindberg, *Ber.*, 1923, **56**, [*B*], 2048; *A.*, ii, 794.
[68] Fr. Auerbach and H. Zeglin, *Z. physikal. Chem.*, 1922, **103**, 161; *A.*, ii, 95.
[69] F. Schulz and S. Landa, *Bull. Soc. chim.*, 1922, [iv], **31**, 1353; *A.*, ii, 96.
[70] A. Kling, *Ann. Chim.*, 1922, [ix], **18**, 189; *A.*, ii, 97.
[71] E. B. Elsbach, *Chem. Umschau*, 1923, **30**, 235; *A.*, ii, 796.
[72] K. W. Rosenmund and W. Kuhnheim, *Z. Unters. Nahr. Genussm.*, 1923, **46**, 154; *A.*, ii, 886.
[73] A. W. Thomas and Chai-Lan Yu, *J. Amer. Chem. Soc.*, 1923, **45**, 113; *A.*, ii, 189.
[74] A. W. Thomas and A. Frieden, *Ind. Eng. Chem.*, 1923, **15**, 839; *A.*, ii, 664.
[75] C. A. Mitchell, *Analyst*, 1923, **48**, 1; *A.*, ii, 188.

The gallotannin used as a standard for this method was practically free from sugar. This was subsequently confirmed, and the fact of the existence of such a tannin must necessarily affect Fischer's conception of gallotannin as a galloyl glucoside.[76]

A new method of estimating reducing sugars by means of Fehling's solution, with the use of methylene-blue as an internal indicator, has been devised, and tables for mixtures of various sugars have been calculated for use with the method.[77] The amounts of cuprous oxide deposited by mixtures of sucrose and reducing sugars have also been worked out and embodied in tables,[78] and a volumetric method of estimating the precipitated cuprous oxide has been devised;[79] also an electrometric method of titrating reducing sugars.[80]

It has been shown under what conditions aldoses are quantitatively oxidised to their corresponding carboxylic acids by an alkaline solution of iodine,[81] and the principle has been applied to the estimation of lactose, dextrose, and lævulose in various preparations.[82]

The method of Willstätter and Schudel,[83] in which dextrose is oxidised to gluconic acid by means of potassium iodide and sodium hydroxide, has not been found accurate in the presence of other sugars.[84]

The iodometric method is also applicable to maltose in the presence of dextrose, lævulose, and sucrose; a period of about thirty-five minutes is required to oxidise the maltose.[85]

For the estimation of mucic acid, a process of oxidation with permanganate and titration of the excess of reagent with oxalic acid gives trustworthy results under specified conditions.[86]

Most of the methods of estimating alkaloids described are modifications of older methods. Nicotine may be accurately estimated by precipitation as silicotungstate.[87]

Reference may also be made to a method of estimating allantoin,

[76] M. Nierenstein, *Ber.*, 1923, **56**, [*B*], 1876; *A.*, i, 1109.
[77] J. H. Lane and L. Eynon, *J. Soc. Chem. Ind.*, 1923, **42**, 32T; *A.*, ii, 193.
[78] H. Jessen-Hansen, *Compt. rend. Trav. Lab. Carlsberg*, 1923, **15**, 21 pp.; *A.* ii, 882
[79] Ed. Lasausse, *J. Pharm. Chim.*, 1922, [vii], **26**, 401; *A.*, ii, 41.
[80] W. L. Daggett, A. W. Campbell, and J. L. Whitman, *J. Amer. Chem. Soc.*, 1923, **45**, 1043; *A.*, ii, 345.
[81] I. M. Kolthoff, *Pharm. Weekblad*, 1923, **60**, 362; *A.*, ii, 346.
[82] *Idem*, *ibid.*, p. 394; *A.*, ii, 346.
[83] R. Willstätter and G. Schudel, *Ber.*, 1918, **51**, 780; *A.*, 1918, ii, 137
[84] G. Bruhns, *Chem. Ztg.*, 1923, **47**, 333; *A.*, ii, 440.
[85] F. A. Cajori, *J. Biol. Chem.*, 1922, **54**, 617; *A.*, ii, 94.
[86] E. O. Whittier, *J. Amer. Chem. Soc.*, 1923, **45**, 1391; *A.*, ii, 589.
[87] O. M. Shedd, *J. Agric. Res.*, 1923, **24**, 961; *A.*, ii, 798.

based on its reaction with Nessler's reagent, to yield mercurous salts insoluble in hydrochloric acid, and subsequent iodometric titration of the solution.[88]

Inorganic Analysis.

Qualitative.—Hexamethylenetetramine, with and without the addition of potassium iodide, is a useful microchemical reagent which forms distinctive crystalline precipitates with the salts of many metals. The test is particularly sensitive in the case of antimony and bismuth.[89]

Several new systematic schemes of separation of metals and acids into groups have been devised. In one of these, the successive group reagents used are (1) magnesium nitrate with ammonia, (2) calcium and ammonium nitrates, (3) barium nitrate, (4) mercuric nitrate, and (5) silver nitrate.[90]

In another scheme acids are divided into the following eight groups: (1) volatile with acetic acid, (2) nitric and boric acid, not volatile with acetic acid, (3) precipitated by barium and calcium acetate, (4) precipitated from ammoniacal solution by barium acetate, (5) by lead acetate, (6) by boiling with lead acetate and ammonia, (7) by nitric acid and silver nitrate, and (8) perchloric, chloric, and bromic acids.[91] A somewhat analogous scheme has also been devised for detecting volatile acids.[92]

The elements precipitated by hydrogen sulphide may be differentiated by the use of spotting tests, with appropriate reagents, on filter-paper.[93]

Peroxides and per-salts may be distinguished by their respective behaviour with an alcoholic solution of *p*-aminophenol, which gives a blue coloration with alkali and barium peroxides, but no coloration with magnesium peroxide or per-salts.[94]

Among the new tests for individual substances is a biochemical one for oxygen, depending on its forming melanin when brought into contact with filter-paper impregnated with worm blood and *l*-β-3 : 4-dihydroxyphenyl-α-alanine.[95]

Isatin can be used as a microchemical reagent for silver and cuprous salts, with which it yields characteristic crystalline precipitates.[96]

[88] J. More, *J. Pharm. Chim.*, 1923, **27**, 209; *A.*, ii, 348.
[89] H. I. Cole, *Philippine J. Sci.*, 1923, **22**, 631; *A.*, ii, 660.
[90] L. Fernandes and U. Gatti, *Gazzetta*, 1923, **53**, i, 108; *A.*, ii, 429.
[91] Z. Karaoglanov and M. Dimitrov, *Z. anal. Chem.*, 1923, **63**, 1; *A.*, ii, 780.
[92] G. Karaoglanov, *ibid.*, 1923, **62**, 217; *A.*, ii, 250.
[93] F. Feigl and F. Neuber, *ibid.*, p. 369; *A.*, ii, 508.
[94] A. Blankart, *Helv. Chim. Acta*, 1923, **6**, 233; *A.*, ii, 338.
[95] H. Schmalfuss, *Ber.*, 1923, **56**, [*B*], 1855; *A.*, ii, 783.
[96] J. B. Menke, *Rec. trav. chim.*, 1923, **42**, 199; *A.*, ii, 150.

A sensitive reaction for cadmium consists in adding potassium thiocyanate and pyridine to an aqueous solution of one of its salts, when a white, crystalline salt, $Cd(C_5H_5N)_2(CNS)_2$, is formed.[97] An analogous compound is formed by zinc.[98]

The chemistry of the Reinsch test has been studied, the composition of the films ascertained, and the conditions for obtaining the best results with arsenic, antimony, and bismuth determined.[99]

A convenient substitute for Bettendorf's reagent for arsenic consists of a solution of calcium hypophosphite in hydrochloric acid; it will detect 0·1 mg. of arsenious oxide.[1]

Nickel may be detected by the formation of a metallic mirror when its solution is treated with ammonia, saturated with hydrogen sulphide, and boiled.[2]

For the microchemical differentiation of potassium and sodium, advantage has been taken of the difference in the crystalline form of the picrates and tartrates of the two metals.[3]

Erratic results sometimes obtained in the brown ring test for nitrates have been found to be due to the reduction of the nitric acid being too slow. This is remedied by adding a drop of dilute hydrochloric acid prior to the sulphuric acid.[4] A new ring test for nitrates and nitrites consists in the formation of a wine-red coloration with certain naphthol- and naphthylamine-sulphonic acids.[5]

By the use of silver nitrate as a reagent, it is possible to detect as little as 0·1 mg. of thiosulphate (S_2O_3),[6] and not less than 0·0001 g. of sulphite (SO_3).[7]

A sensitive test for hydroxylamine depends upon the formation of an unstable purple coloration on treatment with yellow ammonium sulphide and ammonia.[8] Another test is based upon its condensing action on an ammoniacal solution of diacetylmonoxime, to form dimethylglyoxime, which can be readily identified by its well-known reaction with copper.[9]

[97] G. Spacu, *Bul. Soc. Ştiinţe Cluj*, 1922, **1**, 538; *A.*, ii, 879.
[98] *Idem*, *ibid.*, p. 348; *A.*, ii, 699.
[99] B. S. Evans, *Analyst*, 1923, **48**, 357; *A.*, ii, 696.
[1] E. Rupp and E. Muschiol, *Ber. Deut. pharm. Ges.*, 1923, **33**, 62; *A.*, ii, 335.
[2] C. G. Vernon, *Chem. News*, 1923, **126**, 200; *A.*, ii, 342.
[3] Ed. Justin-Mueller, *J. Pharm. Chim.*, 1923, [vii], **28**, 15; *A.*, ii, 656.
[4] C. Faurholt, *Ber.*, 1923, **56**, [*B*], 337; *A.*, ii, 179.
[5] I. G. Nixon, *Chem. News*, 1923, **126**, 261; *A.*, ii, 432.
[6] O. Hackl, *Chem. Ztg.*, 1923, **47**, 210; *A.*, ii, 250.
[7] *Idem*, *ibid.*, p. 466; *A.*, ii, 505.
[8] W. M. Fischer, *ibid.*, p. 401; *A.*, ii, 431.
[9] W. N. Hirschel and J. A. Verhoeff, *Chem. Weekblad*, 1923, **20**, 319; *A.*, ii, 577.

Quantitative.—There have been several new contributions to the methods of determining hydrogen-ion concentration. Among the new indicators described are the colourless carbinols of certain triphenylamine dyes which form coloured ammonium bases on the addition of acid.[10]

The method of Michaelis,[11] in which one-colour indicators are used, with inorganic solutions for comparison, has been found inaccurate, and the constants of the indicators have been redetermined, with the use of Clark's buffer solutions.[12]

Bromoxylenol-blue (dibromoxylenolsulphonephthalein) is a conveniently prepared new indicator with about the same range of p_H value as bromothymol-blue.[13]

A new method in acidimetry and alkalimetry has been based upon the use of certain inorganic salts (lead and silver salts, ferric thiocyanate) instead of a colour indicator. Excess of alkali is added to the acid solution, which is then titrated until the metal hydroxide disappears.[14]

A hydrolytic precipitation method can be used with solutions of compounds of weak acids with strong bases, or vice versa. For example, barium chloride may be titrated in slightly acid solution with potassium chromate, in presence of methyl-red as indicator, the excess of chromate becoming hydrolysed and causing the liquid to become alkaline and affect the indicator.[15]

An alkalimetric method of estimating magnesium and calcium is based on the principle of reducing the solubility of their hydroxides by the addition of another solvent, such as alcohol, so that they no longer affect an appropriate indicator, such as thymolphthalein.[16] It has been found that malic, maleic, and fumaric acids can be readily purified for use as standards in alkalimetry.[17]

Among the new oxidimetric methods is one for the estimation of phosphorous acid in presence of phosphoric acid, by treatment with a cold saturated aqueous solution of bromine, the excess of which is afterwards removed by means of a current of air.[18]

Tellurium dioxide is quantitatively oxidised to tellurium trioxide

[10] L. Karczag and R. Bodó, *Biochem. Z.*, 1923, **139**, 342; *A.*, ii, 694.
[11] *Ibid.*, 1921, **109**, 165; *A.*, 1921, ii, 56.
[12] I. M. Kolthoff, *Pharm. Weekblad*, 1923, **60**, 949; *A.* ii, 694.
[13] A. Cohen, *Biochem. J.*, 1923, **17** 535; *A.*, ii, 779.
[14] K. Jellinek and P. Krebs, *Z. anorg. Chem.*, 1923, **130**, 263; *A.*, ii, 871.
[15] K. Jellinek and J. Czerwinski, *ibid.*, p. 253; A., ii, 878.
[16] R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, 1923, **56**, [*B*] 448; *A.*, ii, 258.
[17] N. A. Lange and H. Kline, *J. Amer. Chem. Soc.*, 1922, **44**, 2709; *A.*, ii, 180.
[18] A. Wingler, *Z. anal. Chem.*, 1923, **62**, 338; *A.*, ii, 506.

by potassium dichromate in hydrochloric acid solution, and a volumetric method of estimating tellurium has been based on the reaction.[19]

Various applications of the use of bromate in volumetric analysis have been studied. A solution of potassium bromate is not decomposed by boiling for five minutes with 2*N*-perchloric, nitric, or acetic acid, so that an excess of the reagent may be used for oxidising purposes under such conditions.[20]

By using a mercuric salt, such as mercuric perchlorate, the reducing action of chlorides, bromides, and iodides upon potassium bromate yields only bromide, whereas in the absence of the mercuric salt free bromine is also formed.[21]

For the estimation of bromate in the presence of ferric iron, an iodometric method may be used, or the bromate may be reduced with sodium oxalate in presence of mercuric perchlorate, and the excess of oxalate titrated with permanganate.[22]

A new reduction method for estimating iron consists in adding a freshly prepared emulsion of zinc sulphide to a hot solution of the ferric salt in sulphuric acid, and subsequently estimating the ferrous iron.[23]

Work on the use of amalgams as reducing agents has been continued,[24] and methods have been devised for their application in the estimation of chromium and iron.[25]

Reference may also be made to a reduction method of estimating persulphuric acid in the presence of hydrogen peroxide and Caro's acid.[26]

The new iodometric methods include one in which the reduction of ferric salts by means of iodides is accelerated by the addition of a cuprous compound, to such an extent that the liberated iodine can be titrated immediately. The principle is also applicable to mixtures of ferric and cupric salts.[27]

Hyposulphites may be estimated by measuring the amount of iodine which they liberate from a solution of potassium iodide and iodate.[28] The conditions for obtaining quantitative results in the reaction between sodium hypochlorite and potassium iodide have

[19] V. Lenher and H. F. Wakefield, *J. Amer. Chem. Soc.*, 1923, **45**, 1423; *A.*, ii, 576.

[20] G. F. Smith, *ibid.*, p. 1115; *A.*, ii, 504.

[21] *Idem*, *ibid.*, p. 1417; *A.*, ii, 573. [22] *Idem*, *ibid.*, p. 1666; *A.*, ii, 650.

[23] P. F. Thompson, *Proc. Australasian Inst. Mining Met.*, 1922, N.S. No. 4, 343; *A.*, ii, 791.

[24] Compare *Ann. Reports*, 1922, **19**, 177.

[25] N. Kano, *J. Chem. Soc. Japan*, 1923, **44**, 37; *A.*, ii, 699.

[26] R. Wolffenstein and V. Makow, *Ber.*, 1923, **56**, [*B*], 1768; *A.*, ii, 652.

[27] F. L. Hahn and H. Windisch, *ibid.*, p. 598; *A.*, ii, 262.

[28] S. H. Wilkes, *J. Soc. Chem. Ind.*, 1923, **42**, 356; *A.*, ii, 698.

also been studied,[29] and applied to the estimation of hypochlorite.[30] For the iodometric estimation of free chlorine in solutions in which it cannot be directly titrated, calcium carbonate is added to the acid liquid, and the resulting gases are led into a solution of potassium iodide.[31]

It has been found possible to use ferric chloride instead of iodine for the estimation of oxidising and reducing agents, the method being based on the reaction

$$2FeCl_3 + Na_2S_2O_3 = 2FeCl_2 + 2NaCl + Na_2S_4O_6.$$[32]

Several new colorimetric methods have been described. For example, bismuth may be estimated by means of the orange colour of colloidal solutions of quinine iodobismuthate;[33] rhodium by the crimson coloration (due to colloidal particles of the metal) developing in an aqueous solution of its salts after boiling with stannous chloride;[34] and tin by means of the molybdenum blue reaction.[35]

For the estimation of small quantities of molybdenum in tungsten advantage has been taken of the blood-red colour of molybdenum thiocyanate.[36]

The conditions under which metallic sulphides volatilise quantitatively when ignited in a current of hydrogen sulphide have been studied, and the results applied to the estimation of lead, bismuth, thallium, antimony, and tungsten; the method cannot be used for tin, nickel, cobalt, or molybdenum.[37] A suitable reduction method for treating the solution before separating arsenic from antimony and tin by distillation of the chloride has been worked out.[38] Arsenic may also be accurately estimated as silver arsenate, either gravimetrically or by decomposing the arsenate with nitric acid and titrating the silver.[39]

Other new precipitants for metals of this group include sodium cyanide for lead,[40] benzoinoxime for copper,[41] and phenylthiohydantoic acid for antimony.[42]

[29] I. M. Kolthoff, *Rec. trav. chim.*, 1922, **41**, 615; *A.*, ii, 176.
[30] *Idem*, *ibid.*, p. 740; *A.*, ii, 176.
[31] E. Kordes, *Z. anal. Chem.*, 1923, **63**, 117; *A.*, ii, 873.
[32] K. Jellinek and L. Winogradoff, *Z. anorg. Chem.*, 1923, **129**, 15; *A.*, ii, 871.
[33] L. Cuny and G. Poirot, *J. Pharm. Chim.*, 1923, **28**, [vii], 215; *A.*, ii, 792.
[34] V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, 1917—18, **49**, 601; **50**, 460; *A.*, ii, 439.
[35] G. F. Hüttig, *Chem. Ztg.*, 1923, **47**, 341; *A.*, ii, 437.
[36] W. J. King, *Ind. Eng. Chem.*, 1923, **15**, 350; *A.*, ii, 342.
[37] L. Moser and E. Neusser, *Chem. Ztg.*, 1923, **47**, 541, 581; *A.*, ii, 580.
[38] K. K. Järvinen, *Z. anal. Chem.*, 1923, **62**, 184; *A.*, ii, 254.
[39] W. Eschweiler and W. Röhrs, *Z. angew. Chem.*, 1923, **36**, 464; *A.*, ii, 787.
[40] W. Herz and E. Neukirch, *Z. anorg. Chem.*, 1923, **130**, 343; *A.*, ii, 879.
[41] F. Feigl, *Ber.*, 1923, **56**, [*B*], 2083; *A.*, ii, 880.
[42] A. and (Mme) A. Lassieur, *Compt. rend.*, 1923, **176**, 1221; *A.*, ii, 438.

Under specified conditions ammonium phosphate can be used to separate bismuth from lead, copper, and cadmium.[43]

Zinc may be estimated by treatment with thiosulphate and pyridine, ignition of the resulting compound $Zn(C_5NH_5)_2(CNS)_2$, and weighing the residual zinc oxide.[44]

For the separation of iron and manganese a new method has been based on the quantitative precipitation of iron from ferric salts by means of "infusible white precipitate," NH_2HgCl, the resulting compound yielding ferric oxide on ignition.[45]

Dinitrosoresorcinol precipitates cobalt quantitatively as the compound $(C_6H_3O_4N_2)_2Co$, and a method of estimating cobalt in the presence of nickel and other metals of the iron group has been based on the reaction.[46]

A new method of estimating nickel consists in precipitating it as oxalate, igniting the precipitate, and weighing the nickel oxide, or by dissolving the precipitate in sulphuric acid and titrating the solution with permanganate.[47]

Magnesium may be separated from the alkali metals by precipitation with guanidine or (less satisfactorily) with piperidine.[48]

New methods of estimating some of the rarer metals have been devised. For example, germanium may be quantitatively precipitated as orthogermanate;[49] praseodymium may be estimated by heating its oxalate in air and weighing the residue of oxide, Pr_6O_{11};[50] and indium may be precipitated as sulphide under specified conditions, and separated from other sulphides by suitable reagents.[51] The methods of estimating potassium by precipitation as perchlorate and cobaltinitrite have been critically examined, and conditions for obtaining quantitative results established.[52]

n-Butyl alcohol has been used as a means of separating the perchlorates of potassium and sodium,[53] and an analogous process has been devised for the quantitative separation of sodium from lithium.[54]

A gravimetric method of estimating nitric acid has been based

[43] G. Luff, *Chem. Ztg.*, 1923, **47**, 133; *A.*, ii, 263.
[44] G. Spacu, *Bul. Soc. Ştiinţe Cluj*, 1923, **1**, 361; *A.*, ii, 580.
[45] B. Solaja, *Chem. Ztg.*, 1923, **47**, 557; *A.*, ii, 583.
[46] W. R. Orndorff and M. L. Nichols, *J. Amer. Chem. Soc.*, 1923, **45**, 1439; *A.*, ii, 584.
[47] W. Löffelbein and J. Schwarz, *Chem. Ztg.*, 1923, **47**, 369; *A.*, ii, 435.
[48] G. Hemming, *Z. anorg. Chem.*, 1923, **130**, 333; *A.*, ii, 878.
[49] J. H. Müller, *J. Amer. Chem. Soc.*, 1922, **44**, 2493; *A.*, ii, 43.
[50] P. H. M.-P. Brinton and H. A. Pagel, *ibid.*, 1923, **45**, 1460; *A.*, ii, 581.
[51] I. Wada and S. Ato, *J. Chem. Soc. Japan*, 1923, **44**, 1; *A.*, ii, 657.
[52] R. L. Morris, *Analyst*, 1923, **48**, 250; *A.*, ii, 698.
[53] G. F. Smith, *J. Amer. Chem. Soc.*, 1923, **45**, 2072; *A.*, ii, 789.
[54] *Idem*, *ibid.*, 1922, **44**, 2816; *A.*, ii, 182.

upon the fact that it combines with di(α-naphthylmethyl)amine to form a nitrate which is only slightly soluble in water.[55]

Electrochemistry.

There has been an exceptionally large number of contributions to the methods of electrochemical analysis. Several new types of apparatus have been described, including one in which oxygen is excluded from the titration vessel,[56] and another in which tubulures for the hydrogen electrode, calomel electrode, and hydrogen inlet are grouped round the burette jet.[57] By the use of an oxygen or air electrode it is possible to titrate an acid or alkali in the presence of potassium permanganate and other oxidising agents.[58]

It is claimed that the use of a bimetallic electrode system composed of two dissimilar metals (for example, certain metals or alloys of the platinum group) gives sharper end-points than those obtained with an ordinary electrode.[59]

Systems comprising two similar metals are of advantage for titrating solutions which may exist in two stages of oxidation; on the other hand, there is a small risk of over-titration.[60] The end-point in the titration of sodium sulphide with ammoniacal silver solution is exceptionally sharp when a bimetallic electrode system is used.[61]

A quinhydrone electrode may be used instead of a hydrogen electrode for the titration of acid solutions, but is unsatisfactory for alkaline solutions unless air is excluded.[62] An antimony electrode is particularly suitable as an indicator for the titration of acids and bases, since it yields salts which are readily dissociated by water and forms an amphoteric hydroxide.[63]

A method of determining the hydrogen-ion concentration of aqueous solutions of carbon dioxide, calcium carbonate, and calcium sulphate by electrometric titration with carbon dioxide gas has been devised, and the bearing of the results obtained with known mixtures of these compounds on the corrosion of iron pipes in earth is discussed.[64]

It has been shown that amino-acids behave like weak acids with-

[55] H. Rupe and F. Becherer, *Helv. Chim. Acta*, 1923, **6**, 674; *A.*, ii, 577.
[56] A. J. Pelling, *J. S. African Chem. Inst.*, 1923, **6**, 40; *A.*, ii, 779.
[57] W. T. Bovie, *J. Amer. Chem. Soc.*, 1922, **44**, 2892; *A.*, ii, 175.
[58] N. H. Furman, *ibid.*, 1922, **44**, 2685; *A.*, ii, 175.
[59] H. H. Willard and F. Fenwick, *ibid.*, 2504; *A.*, ii, 33.
[60] *Idem*, *ibid.*, p. 2516; *A.*, ii, 33.
[61] *Idem*, *ibid.*, 1923, **45**, 645; *A.*, ii, 332.
[62] I. M. Kolthoff, *Rec. trav. chim.*, 1923, **42**, 186; *A.*, ii, 247.
[63] A. Uhl and W. Kestranek, *Monatsh.*, 1923, **44**, 29; *A.*, ii, 648.
[64] J. W. Shipley and I. R. McHaffie, *J. Soc. Chem. Ind.*, 1923, **42**, 311T; *A.*, ii, 649.

out amphoteric character when electrometrically titrated.[65] Of the alkaloids tried, it was found that brucine, quinine, narcotine, and morphine can be estimated by electrometric titration with hydrochloric acid, but that caffeine is too weak a base to show a sharp break in the curve.[66]

Turning next to the new applications of conductimetric methods to precipitation analysis, we find that lithium sulphate can be used for the titration of barium salts and lead salts, but not of calcium and strontium salts;[67] and sodium chromate can be used for the titration of barium, silver, and lead.[68] Silver, lead, and copper may be accurately titrated with lithium oxalate, but magnesium interferes with the titration of calcium.[69]

Owing to the mobility of potassium-ions potassium ferricyanide does not give sharp results as a reagent, and lithium ferricyanide is preferable. It can be used for the estimation of copper, cadmium, nickel, and cobalt.[70] Potassium ferrocyanide is a suitable reagent for the estimation of lead, and for zinc in a weak ammoniacal solution.[71] It may also be used, under specified conditions, for the consecutive titration of zinc and lead in the same solution,[72] and for zinc in the presence of cadmium.[73]

A modification of the electrolytic apparatus of Sand and Hackford[74] for the estimation of arsenic has been devised. Lead electrodes are used, and the procedure described enables 0·001 mg. of arsenious oxide to be detected.[75]

Arsenic and antimony may be estimated together provided both are present in the tervalent condition. Subsequently, the quinquevalent antimony is electrometrically reduced by means of titanous chloride, and then estimated, as before, by means of potassium bromate in hydrochloric acid solution.[76]

To obtain correct results in the electrolytic deposition of antimony, a platinum electrode coated with mercury should be used; with platinum alone there is excessive deposition.[77]

[65] F. M. P. Wildmar and E. L. Larsson, *Biochem. Z.*, 1923, **140**, 284.
[66] W. D. Treadwell and S. Janett, *Helv. Chim. Acta*, 1923, **6**, 734; *A.*, ii, 790.
[67] I. M. Kolthoff, *Z. anal. Chem.*, 1923, **62**, 1; *A.*, ii, 88.
[68] *Idem*, *ibid.*, p. 103; *A.*, ii, 88.
[69] *Idem*, *ibid.*, p. 161; *A.*, ii, 256.
[70] *Idem*, *ibid.*, p. 214; *A.*, ii, 256.
[71] *Idem*, *ibid.*, p. 209; *A.*, ii, 260.
[72] E. Müller and K. Gäbler, *ibid.*, p. 29; *A.*, ii, 90.
[73] F. Müller, *Z. anorg. Chem.*, 1923, **128**, 125; *A.*, ii, 879.
[74] H. J. S. Sand and J. E. Hackford, *T.*, 1904, **85**, 1018.
[75] G. W. Monier-Williams, *Analyst*, 1923, **48**, 112; *A.*, ii, 252.
[76] E. Zintl and H. Wattenberg, *Ber.*, 1923, **56**, [*B*], 472; *A.*, ii, 253.
[77] A. Lassieur, *Compt. rend.*, 1923, **177**, 263; *A.*, ii, 660.

Silver nitrate may be used for the electrometric estimation of zinc, the solution being treated with excess of standard potassium cyanide solution prior to the titration; silver wire is used as the indicator electrode.[78] The same method is also applicable to the estimation of cobalt by means of silver nitrate.[79]

Ferrous salts and quadrivalent vanadium salts may be successively titrated electrometrically with potassium permanganate in the same solution, the former being more vigorous reducing agents than the latter.[80] The method may also be used for mixtures of salts of iron, uranium, and vanadium after reduction with zinc and sulphuric acid, but air must be excluded during the titration of the vanadium.[81]

The conditions for the electrometric oxidation of halides to their respective cyanides by means of potassium permanganate in hydrocyanic acid solution have been determined for the mixed salts. In the case of iodides, oxidation to iodate by means of alkali hypobromite, and electrolytic estimation of the excess of reagent by means of arsenite, is more accurate than the cyanide method.[82] Another electrometric method depends upon the liberation of the halogens and their successive separation by boiling the solution.[83] Methods have also been devised for the electrometric titration of halides, cyanides, sulphides, and thiosulphates, with the use of a mercury electrode.[84]

Electrometric titration with titanous chloride in acid solution affords an accurate means of estimating iodates, bromates, chlorates, and ferricyanides.[85]

The same reagent is also applicable to the electrometric titration of selenium in quantities not exceeding 0·1 mg. in cold solution. Under these conditions, tellurium is not reduced.[86]

Water Analysis.

Attention has been directed to the contamination of samples of water when stored in bottles of bad glass. Within a week,

[78] E. Müller and A. Adam, *Z. Elektrochem.*, 1923, **29**, 49; *A.*, ii, 260.
[79] E. Müller and H. Lauterbach, *Z. anal. Chem.*, 1923, **62**, 23; *A.*, ii, 92.
[80] E. Müller and H. Just, *Z. anorg. Chem.*, 1922, **125**, 155; *A.*, ii, 42.
[81] R. G. Gustavson and C. M. Knudson, *J. Amer. Chem. Soc.*, 1922, **44**, 2756; *A.*, ii, 185.
[82] H. H. Willard and F. Fenwick, *J. Amer. Chem. Soc.*, 1923, **45**, 623; *A.*, ii, 331.
[83] G. Schay, *Z. Elektrochem.*, 1923, **29**, 123; *A.*, ii, 331.
[84] I. M. Kolthoff and E. J. A. H. Verzyl, *Rec. trav. chim.*, 1923, **42**, 1055; *A.*, ii, 873.
[85] W. S. Hendrixson, *J. Amer. Chem. Soc.*, 1923, **45**, 2012; *A.*, ii, 781.
[86] H. H. Willard and F. Fenwick, *ibid.*, p. 933; *A.*, ii, 430.

sufficient mineral matter may be dissolved to alter the character of the water, notably in its silica and soda content.[87]

A rapid gasometric method of estimating the dissolved oxygen and nitrogen in water has been described, the gases being liberated by dissolving a highly soluble substance, such as potassium hydroxide, in the water.[88]

A new formula has been devised for calculating the active carbon dioxide (c) in drinking water from the total carbon dioxide (t) in mg. per litre: $c = 27[\sqrt[3]{t} - \sqrt{t^2 + 5823}]$, a correction being required where the value of t exceeds 200 mg.[89]

In estimating carbonates in mineral waters, it is necessary to eliminate any sulphide present, for example, by means of lead peroxide followed by hydrogen peroxide, and to filter the liquid after heating it for thirty minutes at 45°.[90] The total iodine in mineral waters containing sulphides may be rapidly estimated by oxidising organic matter and sulphides with alkaline permanganate, liberating the halogens with sulphuric acid, absorbing the iodine in carbon disulphide, and estimating it colorimetrically.[91]

A new reagent for the detection of nitrites in water by means of a zone test consists of a 6 per cent. solution of resorcinol in pure sulphuric acid. The intensity of the coloration (pale rose to brownish-black) at the zone of contact enables an approximate estimation of the nitrous acid present to be made.[92]

The yellow coloration produced by ammonium molybdate with silica has been used for the colorimetric estimation of silica in water, and enables colloidal silica to be differentiated from non-colloidal silica, which is the form of usual occurrence in water.[93]

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[87] W. D. Collins and H. B. Riffenburg, *Ind. Eng. Chem.*, 1923, **15**, 48; *A.*, ii, 83.

[88] H. G. Becker and W. E. Abbott, *Sci. Proc. Roy. Dublin Soc.*, 1923, **17**, 249; *A.*, ii, 784.

[89] P. Lehmann and A. Reuss, *Z. Unters. Nahr. Genussm.*, 1923, **45**, 227; *A.*, ii, 697.

[90] F. Touplain and J. Dubief, *Ann. Falsif.*, 1923, **16**, 76; *A.*, ii, 337.

[91] J. Dubief, *ibid.*, p. 80; *A.*, ii, 332.

[92] G. Rodillon, *J. Pharm. Chim.*, 1922, [vii], **26**, 376; *A.*, ii, 37.

[93] F. Diénert and F. Wandenbulcke, *Compt. rend.*, 1923, **176**, 1478; *A.*, ii, 507.

PHYSIOLOGICAL CHEMISTRY.

THIS year it has been decided, in view of the large amount of work which should be reviewed, to omit that portion of the Report which in previous years has been devoted to *personalia* and notices of new books.

A survey of the literature published during the past year leaves a reporter little choice other than to deal to a large extent with the subjects that were reviewed at the end of 1922.

It is of interest to note that the work reviewed in the following pages includes the researches for which no fewer than four of the recently awarded Nobel Prizes were given. The 1923 Prize for Medicine was awarded to Dr. F. G. Banting and Prof. J. J. R. Macleod, of Toronto, for their researches on insulin, whilst, by a happy choice, the complementary researches of Prof. A. V. Hill and of O. Meyerhof on the mechanism of muscular contraction were selected for a second joint award in 1922.

The Internal Secretion of the Pancreas.

In last year's Report the discovery of the long-sought internal secretion of the pancreas by the Canadian investigators F. G. Banting and C. H. Best was described. It is not surprising that the announcement of a discovery of such importance has been followed by a great deal of experimental work. Indeed, the task of reviewing the literature which has appeared during the past twelve months on this subject has proved to be no easy matter, particularly when it was soon apparent on perusal that much that has been published does not represent careful work or mature consideration. In the first place, chemists will naturally be interested to learn of the progress that has been made towards a recognition of the nature of "insulin." For some months after the discovery of insulin it was usual to prepare it by the original method described by Collip.[1] This method was a somewhat tedious fractional precipitation by means of alcohol, and yielded a preparation, usually referred to now as "crude insulin," which was a white, hygroscopic powder. The yield varied considerably, but averaged 0·7 gram per kilo. of fresh pancreas, and its potency, measured in terms of the original Toronto unit of standardisation,

[1] *J. Biol. Chem.*, 1923, **45**, *Proc. Amer. Soc. Biol. Chem.*, xl.

that is, the dose required to lower the concentration of the blood-sugar of a 2-kilo. rabbit, which has fasted for sixteen to twenty-four hours, from a normal value of 0·1 per cent. to about 0·04 per cent., and to induce typical hypoglycæmic convulsions within four hours, was represented by a dosage of about 7 mg. Obviously, from its method of preparation, such material contained very much that was not the active substance, and several investigators have published improved methods. Perhaps the most important of these practical improvements has been that advised by Dudley.[2] He found that "crude insulin" made by Collip's original method contains nearly 50 per cent. of inorganic salts, and that it gave positive reactions with such diverse tests as biuret, Millon, glyoxylic acid, Pauly, Molisch, Selivanov, and the test for organic sulphur. Furthermore, he found that the hormone is precipitated from aqueous solution by a variety of reagents, such as uranium acetate, phosphotungstic acid, and, in particular, picric acid. The compound with the last-named substance is a lemon-yellow powder, which is only slightly soluble in water, but can readily be converted into a soluble hydrochloride. The "hydrochloride" is an almost white powder which is readily soluble in water. As it is not hygroscopic, it can be kept more readily than "crude insulin," whilst its activity, weight for weight, is approximately ten times that of the original material. A similar method is used by Sordelli and Deulofeu.[2a]

It is clear that this improved method of preparation has given us a much cleaner product than "crude insulin," but it is equally obvious that we are not yet dealing with the hormone in a pure state. The "hydrochloride" no longer shows positive tests for the presence of phosphorus, which is in agreement with the observations of Doisy, Somogyi, and Shaffer,[3] who prepared their insulin by precipitating it at its isoelectric point, p_H 5, nor does it give a positive Selivanov test for fructose, in this respect differing from the preparations made by Winter and Smith[4] from pancreas and from yeast. Of the reactions mentioned above, the only ones given to a marked degree by the "hydrochloride" are the Pauly reaction for the iminazole ring, the biuret test, and the test for organic sulphur. These are properties which would reasonably be given by a protein derivative, and such an idea of the nature of insulin is supported by Dudley's further observations that both pepsin and trypsin destroy the activity of insulin "hydro-

[2] *Biochem. J.*, 1923, **17**, 376; *A.*, i, 967.
[2a] *Compt. rend. Soc. Biol.*, 1923, **89**, 743.
[3] *J. Biol. Chem.*, 1923, **55**, *Proc. Amer. Soc. Biol. Chem.*, xxxi.
[4] *Proc. Physiol. Soc., J. Physiol.*, 1923, **57**, xl; *A.*, i, 513.

chloride." These facts, together with the results of experiments which show that the active principle is readily destroyed by alkali, and that it is quickly adsorbed from acid solution by filtration through a Berkefeld filter, although not from weakly alkaline solutions, have led Dudley to conclude that insulin may be a very complex protein derivative. This view is supported by Widmark,[5] who has made a study of the solubilities of insulin, but his support loses much of its value because he employed a crude preparation, and also by Witzemann and Livshis.[5a] The observations of Best and Macleod[6] are not in agreement with this opinion, for they find that whereas insulin prepared from ox or pig pancreas may give certain protein reactions, that prepared from the skate does not, and furthermore, by employing phosphotungstic acid the protein matter may be separated from insulin prepared from ox or pig pancreas without impairing its activity.

Recent papers by Piper, Allen, and Murlin,[7] and by Kimball and Murlin[8] also contain evidence that insulin is not a protein derivative.

Bearing in mind that there is general agreement on the ease with which insulin is carried down from solution by adsorbents, it is reasonable to suppose that many of the preparations described are adsorption complexes of insulin with complexes of a protein nature. Its destruction by the proteolytic enzymes pepsin and trypsin recorded by Dudley and others is not, however, explained by this view.

The discovery of insulin was soon followed by the commercial preparation of this material on a large scale for therapeutic use. As is now well known, the preparation in this country was controlled by the Medical Research Council, and there can be no doubt that this action, much criticised at the time, protected the public from being exploited in a manner which might have had serious consequences. The manufacture of insulin by trustworthy makers only has led to the results of its widespread clinical use being in general highly satisfactory. Naturally, the supply of pancreas is a limiting factor on the output, and there have been curiously interesting developments as a result of the search for other possible sources of insulin.

J. B. Collip, one of the original team of the Toronto workers, impressed with the relation between the power of the liver to form glycogen and the pancreatic hormone, was led to suspect that

[5] *Biochem. J.*, 1923, **17**, 668; *A.*, i, 1148.
[5a] *J. Biol. Chem.*, 1923, **57**, 425; *A.*, 1924, i, 108; *ibid.*, **58**, 463.
[6] *Amer. J. Physiol.*, 1923, **63**, 390.
[7] *J. Biol. Chem.*, 1923, **58**, 321. [8] *Ibid.*, p. 337.

wherever glycogen occurs there will be found a hormone similar in its action to the pancreatic substance. Accordingly, he investigated two sources, which, if this hypothesis were correct, should yield such a hormone. There were, in the first place, certain lower animals such as the clam, and secondly certain yeasts and other fungi, in all of which glycogen is formed in relatively large amounts. From the tissues of the clam (*Mya arenaria*) a substance was prepared [9] which definitely produced a fall in the concentration of blood-sugar in animals, but only after a latent period of from one to four days after injection. This result he explained by postulating the slow activation of an inactive precursor. In the same manner, Collip [10] has prepared an active substance from yeasts, although at first many failures were recorded. The administration of the material from yeast sometimes gave rise to an immediate hyperglycæmia, followed later by hypoglycæmia in from five to sixty-five hours. Of even more importance is the observation that the blood-sugar level of a depancreatised dog could be reduced by the administration of the yeast preparations. Simultaneously with Collip's announcement, a similar claim was advanced by Winter and Smith, working in the Cambridge Laboratory.[11] Hutchinson, Smith, and Winter,[12] and Funk and Corbitt [12a] also note a variability in the activity of preparations made from yeast, and the former state that micro-organisms other than yeast can yield substances which reduce the concentration of sugar in the blood. Having traced an apparent association between glycogen and a substance resembling insulin in a plant, yeast, Collip [13] directed his attention to the theory regarding the action of insulin which had been advanced by Winter and Smith (compare *Ann. Reports*, 1922, p. 195). Collip reasoned that if insulin is concerned in the animal organism with the conversion of a mixture of α- and β-glucose into the more reactive γ-glucose, then a similar hormone should be an essential constituent of any plant which breaks down dextrose. This train of thought should lead to the logical conclusion that all living tissues require the co-operation of such a hormone, but it induced him to examine the onion, as typical of a plant which oxidises glucose and does not form starch. The onion extracts were found to induce the same type of physiological effects in animals as did the extracts from yeast.

[9] *J. Biol. Chem.*, 1923, **55**, *Proc. Amer. Soc. Biol. Chem.*, xxxix.
[10] *Ibid.*, 1923, **56**, 513; *A.*, i, 967.
[11] *Proc. Physiol. Soc., J Physiol.*, 1923, **57**, xl; *A.*, i, 513.
[12] *Biochem. J.*, 1923, **17**, 683, 764.
[12a] *Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 422.
[13] *J. Biol. Chem.*, 1923, **56**, 513; *A.*, i, 967.

Best and Scott [14] also record the preparation of active extracts from wheat, beet, and celery, whilst Collip [15] has also used barley tops, sprouted grain, green wheat leaves, bean tops, and lettuce. That plant extracts from various sources can depress the blood-sugar level both in normal animals and in depancreatised dogs would therefore appear to be definitely established. In view of the fact that the effects develop much more slowly than when insulin is used, it is possible that the factors are not identical with the hormone of the pancreas, and on these grounds Collip proposes for them the name glucokinin.[16] Dubin and Corbitt [16a] have recently furnished evidence that in such plant extracts there are present two factors, one producing hyperglycæmia, and the other, which resembles insulin, producing hypoglycæmia. By suitable means these two substances may be separated, and it is then found that the latter factor is probably identical with insulin from the pancreas. These investigators attribute the slow action of plant extracts in reducing blood-sugar on injection to the inhibitive effect of the substance causing hyperglycæmia. The therapeutic value of plant extracts has not yet been sufficiently examined to enable an opinion to be formed, but if it should be found possible to employ them, a very big advance will have been made. In favour of their possible employment for human use is the fact that, although the physiological effects of their administration develop more slowly than in the case of insulin, they are maintained for a much longer time.

In connexion with the therapeutic administration of insulin, which is by injection, it is possible that important improvements may follow the statement by Winter [17] that the hormone may be absorbed from the stomach when administered by the mouth in the form of weak alcoholic solutions, although this has not been confirmed by Harrison.[17a]

Turning now to the important question of the actual significance of insulin in relation to carbohydrate metabolism, we find that, in spite of a certain amount of somewhat rash speculation in certain quarters, steady progress is being made towards its solution. In last year's *Report* (p. 195) reference was made to Winter and Smith's hypothesis that the sugar in the blood of diabetics is a mixture of α- and β-glucose which must be transformed into a more reactive form—possibly the ethylene oxide or γ-glucose—before it can be oxidised in the organism. This hypothesis, which has received little or no support, has now been extended by these

[14] *J. Metabolic Res.*, 1923, **3**, 177. [15] *Nature*, 1923. **111**, 571; *A.*, i, 728.
[16] *J. Physiol.*, 1923, **58**, 18. [16a] *Proc. Soc. Exp. Biol. Med.*, 1923, **21**, 16.
[17] Winter and Smith, *Brit. Med. J.*, 1923, i, 711.
[17a] *Brit. Med. J.*, 1923, Dec. 22.

investigators [17, 18] so as to allocate a rôle to insulin, although it must frankly be admitted that the experimental evidence in support of their conclusions is somewhat inadequate.[18a] They claim to have shown the presence of an enzyme in the liver which will cause certain changes in the rotation shown by dextrose and lævulose solutions in the presence of small amounts of insulin. These changes were not observed when boiled liver-tissue was employed. The view of these workers, that sugar is present in normal blood as the highly reactive γ-glucose, was referred to in last year's *Report*, and doubt was then expressed as to the adequacy of the evidence on which this theory was advanced. The work published during the ensuing twelve months has not caused the reporter to change his opinion. The results of Hewitt and Pryde,[19] on which this theory was largely based, have been challenged by Stiven and Reid [20] and by van Crefeld [20a] whereas one of the former observers [21] has himself raised strong objection not only to the technique employed by Winter and Smith, but also to their interpretations of the results. The differences that occur between the results of estimations of sugar in blood by polarimeter and by copper-reducing methods which first led Winter and Smith to advance their theories have also been noted by Stepp,[22] particularly in the case of bloods from diabetics. From a study of this relation of the polarimetric value to the copper-reducing value, as they may for convenience be termed, of diabetic blood extracts before and after acid hydrolysis, Winter and Smith believe they have obtained evidence of the presence of a complex carbohydrate in the blood in this disease.[23] They also find that the injection of insulin into diabetics causes a breakdown of this complex carbohydrate.[24] Furthermore, the injection of adrenalin into normal rabbits, in their opinion, changes the normal sugar of the blood into something resembling this complex carbohydrate present in diabetic blood. In the blood of normal animals which had received injections of insulin until convulsions appeared, the same authors claim to have detected the presence of a dextrorotatory carbohydrate without copper-reducing power.[25] One cannot help expressing regret that so much of this work would appear to have been published in an immature condition.

The relation between the amount of sugar utilised by the

[18] *Proc. Physiol. Soc., J. Physiol.*, 1923, **57**, xiii.
[18a] See Alles and Winegarden, *J. Biol. Chem.*, 1923, **58**, 225.
[19] *A.*, 1920, i, 508. [20] *Biochem. J.*, 1923, **17**, 556; *A.*, i, 1153.
[20a] *Ibid.*, 860. [21] J. A. Hewitt, *Brit. Med. J.*, 1923, i, 590; *A.*, i, 973.
[22] *Ergeb. Physiol.*, 1922, **20**, 108.
[23] *Proc. Physiol. Soc., J. Physiol.*, 1923, **57**, xxxi; *A.*, i, 513.
[24] *Brit. Med. J.*, 1923, i, 711. [25] *Nature*, 1923, **111**, 810; *A.*, i, 727

organism and that of insulin administered was, both from early experiments on animals and from clinical trials, recognised as a quantitative one, and this is of considerable importance from the point of view of the physiological standardisation of insulin. McCormick, Macleod, Nobel, and O'Brien,[26] as well as other investigators, have pointed out that the amount of glycogen present in the test animal has a distinct influence on the dose of insulin which is required to produce the requisite fall in concentration of the blood-sugar and the typical convulsions; hence the importance of employing as test subjects only those animals which have previously had their glycogen reserves depleted by twenty-four hours' starvation.

The most natural question that came to one's mind when one heard that insulin causes a diminution of the blood-sugar in the animal organism, so that by careful regulation a diabetic can be restored to all intents and purposes to normal health, was to inquire as to the fate of the sugar that disappears. Since the diabetic may with properly regulated insulin treatment gain markedly in weight, and exhibit an almost normal carbohydrate tolerance, it might reasonably be expected that the sugar is oxidised along the normal paths of metabolism. However, Dudley, Laidlaw, Trevan, and Boock[27] have shown by determinations of the respiratory quotient that the injection of insulin does not apparently directly increase the rate of combustion of dextrose, and confirmatory results were obtained by Kellaway and Hughes[28] in a study of the effect of insulin administration on the respiratory metabolism of a normal human subject. If this does not occur, then the possibility that the sugar leaving the blood goes to form glycogen at once suggests itself. Dudley and Marrian[29] find, however, in such animals no increase in the glycogen reserves in the liver or the skeletal muscles. If the sugar leaves the blood and is neither oxidised nor converted into glycogen, there is then the possibility to be considered that it is transformed into fat, but Dudley and Marrian could find no evidence that this occurs. McCormick, Macleod, O'Brien, and Nobel[30] believe that insulin causes what they call a "glucose vacuum" in the tissue-cells, which accordingly withdraw the sugar faster from the blood than it is being formed from glycogen. Nevertheless, its fate after absorption by the cell is still the subject of some speculation. Dale[31] believes it not improbable that as in complete pancreatic

[26] *J. Physiol.*, 1923, **57**, 234; *A.*, i, 514.
[27] *Proc. Physiol. Soc., J. Physiol.*, 1923, **57**, xlvii.
[28] *Brit. Med. J.*, 1923, **1**, 710; *A.*, i, 972.
[29] *Biochem. J.*, 1923, **17**, 435; *A.*, i, 978.
[30] *Amer. J. Physiol.*, 1923, **63**, 389.
[31] *Lancet*, 1923, **1**, 992.

diabetes the organism cannot burn sugar, so in the state produced by excess of insulin there is the direct antithesis, and the body is living on nothing but sugar. This explanation would appear to agree with certain of the experimental observations. Thus, the first effect of a large dose of insulin should be to cause a sharp rise in the respiratory quotient, which actually occurs, and would not necessarily be accompanied by an increase in general metabolism. Later, as the supply of sugar begins to run low, the metabolism should fall rapidly, until, when the blood-sugar reaches a certain level, the failing combustion of this substance would be overtaken by the metabolism of fat and protein and the respiratory quotient would reach the values far below normal which are obtained. The Cambridge group of investigators have recorded that the inositol content of rats is increased after convulsions caused by insulin,[32] and also that there is a rapid fall in the inorganic phosphates which persists for many hours after recovery from the convulsions.[33] The significance of these changes is as yet not clear, although the authors advance somewhat tentative explanations. The conclusion drawn from studies of the respiratory exchange that insulin does not cause an increased oxidation of sugar is supplemented by the observations of Eadie, Macleod, and Noble[34] that the rate of glycolysis in shed blood or the excised liver[35] is unaffected by insulin. Thalhimer and Perry,[36] however, believe that the low glycolytic power of diabetic blood can be raised to a normal value by insulin administration, although they agree that no such effect can be observed *in vitro*. Azuma and Hartree[36a] could detect no influence of insulin on the heat production of isolated frog's muscle.

Noble and Macleod[37] record the interesting fact that dextrose and mannose are the only sugars of a number tested which bring about a disappearance of the characteristic symptoms of insulin administration. Arabinose, xylose, sucrose, lactose, sodium lactate, glycerol, ethyl alcohol, and alkalis had no effect.

What may prove to be a discovery of the first degree of importance is recorded by Burn,[38] who finds that the subcutaneous administration of pituitary extract diminishes or abolishes the hypoglycæmia produced by insulin. Indeed, the convulsions associated with insulin hypoglycæmia can be dispelled as rapidly by pituitary extract as by dextrose. In this connexion it is interesting to recall

[32] Needham, Smith, and Winter, *J. Physiol.*, 1923, **57**, lxxxii.
[33] Wigglesworth, Woodrow, Smith, and Winter, *J. Physiol.*, 1923, **57**, 447.
[34] *Amer. J. Physiol.*, 1923, **65**, 462; *A.*, 1924, i, 113.
[35] Noble and Macleod, *J. Physiol.*, 1923, **58**, 33.
[36] *J. Amer. Med. Ass.*, 1923, **80**, 1614.
[36a] *Biochem. J.*, 1923, **17**, 875.
[37] *Amer. J. Physiol.*, 1923, **64**, 547.
[38] *J. Physiol.*, 1923, **57**, 318.

that cases of pituitary insufficiency frequently exhibit a raised carbohydrate tolerance. In direct relation to these results are those obtained by Olmsted and Logan,[39] who find that decerebrate cats with intact pituitary maintain a high blood-sugar level which is not much reduced by insulin. If the pituitary is removed, insulin provokes typical convulsions. Decapitated cats may have the blood-sugar level lowered by insulin below that at which convulsions appear in normal cats without obtaining convulsions.

Internal Secretions of Pituitary and Thyroid Gland.

Another careful attempt has been made by Dudley[40] to isolate the active principle of the pituitary gland, but, unfortunately, without success. The greater part of the uterine stimulant may be concentrated in the material dissolved by ethyl alcohol from the butyl alcohol extract of the powdered glands.[41] From this fraction an active crystalline picrate was eventually isolated, but proved on purification to be the double salt of creatinine and potassium. The mother-liquors from the crystallisation of this salt showed marked activity, and could be further separated into two fractions by means of acetone. The insoluble fraction consisted of a dry powder with an activity on the isolated uterus about twelve times as great as that of histamine, and showed a simple pressor effect on blood pressure. The constituents of the soluble fraction, which was a deliquescent resin, showed a smaller uterine activity, and a pressor effect on blood pressure, which was preceded by a depressor effect. Dudley believes that at least three distinct active principles are present in pituitary extracts, a view which is not accepted by Abel and Rouiller,[42] who regard the oxytocic principle as probably identical with the pressor and diuretic principles. In a recent publication,[43] the latter authors describe in a preliminary manner the separation, after a long fractionation, of what they appear to regard as the active principle in the form of a tartrate. This preparation is stated to have an activity 1,000 to 1,250 times greater than that of histamine, whilst the doses necessary to raise the blood pressure by an appreciable degree in cats, and to cause marked diuresis in rabbits, are respectively 1/100 and 1/20 of a milligram. This preparation is undoubtedly highly potent, but in the light of Dudley's experience, and of the admission by Abel and Rouiller themselves that the active principle is readily adsorbed, and that the chemical purity

[39] *Amer. J. Physiol.*, 1923, **66**, 437.
[40] *J. Pharm. Exp. Ther.*, 1923, **21**, 103; *A.*, i, 629.
[41] *A.*, 1920, i, 344.
[42] *J. Pharm. Exp. Ther.*, 1922, **20**, 65.
[43] Abstract of Communications to XIth Intern. Congress Physiol. Edinburgh, 1923.

of their tartrate has not yet been established, it would seem wise to reserve judgment on this matter.

The announcement by Romeis [44] of the isolation of the thyroid hormone may be mentioned here as recalling Kendall's isolation of thyroxin.[45] Romeis separates his material in the form of a precipitate obtained by acidifying the products of hydrolysis of thyroid gland after boiling with barium hydroxide solution until there is no response in the biuret test. The crude material thus obtained is purified by repeated dissolution in alkali and precipitation with acid. Extraction of this product with acidified alcohol yields a fraction which is further purified by extraction and precipitation. Finally, a light brown powder with a high iodine content is obtained, which is stated to be a substance resembling, and probably related to, Kendall's thyroxin. Although it shows marked physiological activity, one is led to question whether products prepared by such drastic methods can bear any direct relation to the active principles of the gland. There is a regrettable tendency to announce the separation from thyroid tissue of any substance with a high iodine content as the isolation of the active principle. It can be recalled that not only was a structural formula advanced for Kendall's thyroxin, but also that Osterberg claimed to have on at least two occasions (1917, 1919) effected its synthesis.[46] As yet no details of this important achievement have been forthcoming.

Fat-soluble Vitamins and Calcification of Cartilage.

Although this subject has been dealt with at some length in several previous Reports, the results achieved during the past twelve months are of such importance that they cannot well be passed over. Perhaps the most striking publication of the year has been the report of the investigations on rickets in Vienna during 1919—1922,[47] in which is described the work of Dr. Hariette Chick and her colleagues. This report deals with the practical application on a large scale of the dietary theory of the etiology of rickets advanced some years ago by Mellanby,[48] and the results described therein should dispel any doubts which might remain as to the truth of Mellanby's main contentions. A most striking feature of this report is the preface written by Prof. C. von Pirquet, the eminent authority on nutrition, who provided Miss Chick with the facilities for her investigation. He records how after closely watching the experiments throughout their course he finally became

[44] *Biochem. Z.*, 1922, **13**, 3, 97; *A.*, *i*, 267.
[45] *Ann. Reports*, 1919, p. 159. [46] *Ibid.*, 1919, 1920.
[47] Medical Research Council, Special Report, No. 77, 1923.
[48] *Ibid.*, No. 61, 1921.

convinced, not only that rickets is a disease of nutrition, but also that a deficiency of fat-soluble vitamins in the diet is an essential cause of the disease. It will be remembered that Mellanby traced a close parallel between the distribution of the organic factor which exerted an anti-rachitic action, and that of the substance known as vitamin-*A*, although he was careful not to assume their identity. In 1921 McCollum, Simmonds, Shipley, and Park [49] expressed the view that the anti-rachitic substance is distinct from the vitamin-*A*, and in last year's Report the reporter expressed the opinion that these workers might possibly not have considered the matter sufficiently from the quantitative point of view. Later work by McCollum and his co-workers, as well as by Goldblatt and Zilva,[50] has now provided satisfactory evidence that the anti-rachitic and growth-promoting factors are distinct. Although both substances are present in cod-liver oil, they are destroyed at markedly different rates by oxidation; furthermore, certain foodstuffs, for example, spinach, may serve as valuable sources of one substance without providing appreciable amounts of the other.

The newly discovered substance may provisionally be termed the anti-rachitic vitamin, as an attempt to term it vitamin-*D* has led to some confusion with another recently discovered substance in yeast, for which Funk has reserved this name. The Vienna experiments again emphasise the importance of light in the prevention and cure of rickets. When last year's Report was written, it was uncertain whether or not exposure to short wave-length radiation could actually replace the fat-soluble vitamins in bringing about satisfactory growth and bone formation. This point has now been satisfactorily cleared up by the work of Hume,[51] and of Goldblatt and Soames,[52] who agree that the radiation will not render the fat-soluble vitamins dispensable, but may, however, enable an animal to economise to no small degree its supply of these substances, so that an animal on a diet deficient in the fat-soluble vitamins will thrive much longer if irradiated than if it were not so treated. Very interesting too has been the claim by Hume and Henderson Smith [53] to have produced this same effect, not by radiating the animals themselves, but by maintaining them in vessels containing air which had previously been irradiated. Replacing the irradiated air in the jars by ordinary air or by ozone caused the effect to disappear. In attempting an explanation of this most curious observation, one naturally thinks of ionised air or oxides of nitrogen as possibly being the active substances formed

[49] *A.*, 1921, i, 757. Also *Amer. J. Hyg.*, 1921, **1**, 512.
[50] *Lancet*, 1923, ii, 647. [51] *Ibid.*, p. 1318. [52] *Ibid.*, p. 1321.
[53] *Biochem. J.*, 1923, **17**, 364.

by the radiation, but in view of the failure of Webster and Hill [54] to confirm the main results of Hume and Smith, it may be well to postpone further discussion.

Regarding the nature of the organic factors in cod-liver oil, no further work of outstanding interest has been published on the nature of the anti-rachitic substance. The vitamin-*A*, which is now supposed to be mainly concerned with the growth processes, has, however, been further investigated. K. Takahashi and Kawakami [55] have described the preparation from cod-liver oil of a substance which they claim to be the vitamin-*A* in a semi-crystalline and nearly pure condition. From a close survey of the description they have published it would appear doubtful that they have actually got anything approaching a pure substance. It is stated to contain only carbon, hydrogen, and oxygen, and to resemble an aldehyde in its properties. It shows the general solubilities of fatty substances.

Although it is generally recognised now that one or more unidentified organic factors, such as are now loosely termed the fat-soluble vitamins, play an essential part in normal calcification of cartilage, we are entirely ignorant as to their rôle. Turning, however, to the actual mechanism of calcium deposition, we find encouraging progress to report. Until recently, the process by which calcium salts are deposited in cartilage to form bone has been regarded very much as if it were purely a physico-chemical problem. Thus for a number of years Freudenberg and György [56] have investigated the influence of various conditions on the absorption of calcium salts from solution by pieces of cartilage *in vitro*. The results, whilst interesting in themselves from the point of view of colloid chemistry, cannot be said to have advanced to any appreciable extent our knowledge of the process of calcification as it occurs in the body. Indeed, Watt [57] has shown that the crystalline forms in which calcium carbonate and calcium phosphate are deposited from aqueous or colloidal solutions are dissimilar from the deposits in bone. A clue to this difficult problem has, however, been provided from a most unexpected quarter, and it is one which bids fair to solve many of the major difficulties. In investigating the products of fermentation of sugar by yeast, Harden and Robison [58] described the presence of a hexosemonophosphoric ester. The compound was isolated by Robison and described by him in a recent paper.[59] It is entirely different from

[54] *Proc. Physiol. Soc., J. Physiol.*, 1923, **57**, lxxvii.
[55] *J. Chem. Soc. Japan*, 1923, **44**, 580; *A.*, i, 968.
[56] See *Ann. Reports*, 1921, p. 187.
[57] *Biol. Bull.*, 1923, **44**, 280; *A.*, 1924, i, 119.
[58] *P.*, 1914, **30**, 16.
[59] *Biochem. J.*, 1922, **16**, 809; *A.*, i, 86.

the compound prepared by Neuberg,[60] and yields calcium and barium salts which are readily soluble in water. Robison was led to investigate the action of enzymes on solutions of these salts, and found that in some cases the ester was hydrolysed. In such cases the progress of the hydrolysis was shown by the deposition of sparingly soluble calcium or barium phosphate. These results at once suggested to him the possibility that such a soluble calcium salt might be the form in which the mineral could be carried to ossifying cartilage, there to be broken down by an appropriate enzyme into calcium phosphate and free sugar. Experiments soon proved that ossifying cartilage of young animals actually possesses the power rapidly to hydrolyse this hexosemonophosphoric acid, whereas of all other tissues the only one showing this power to any significant degree is the kidney.

The difficulties of explaining the deposition of calcium in cartilage and not in other tissues has in the past led to all sorts of suggestions, such as the specific adsorption of ions (Pfaundler [61]), whilst the fact that serum contains more calcium salts in solution than can be carried in the form of calcium phosphate or carbonate by the same volume of water has also given rise to much speculation. It must be remembered that Cushny [62] found that when serum is filtered through collodion all the crystalloids pass through except some of the calcium and magnesium, and also that many investigators have recorded the presence in blood of a certain amount of organically-combined phosphoric acid in a form readily hydrolysed by acids.[63, 64] If it can be shown that blood contains the calcium salt of a hexosephosphoric acid such as Robison has studied, the importance of his discoveries may indeed be far-reaching.

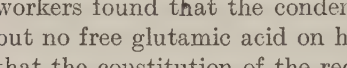
Perhaps not unconnected with these results are the observations that in rickets there may be a decreased amount of calcium and phosphorus in the blood.[65] Hess and Lundagen [66] note that there may be seasonal variations in the amounts present in children's blood, and that minimum values are usually observed in March, when also the incidence of rickets is at its height. The values may rapidly be brought again to normal by exposure of the child to short wave-length radiation, or by administration of cod-liver oil.[67, 68] As an attempt to explain the beneficial action of radiation

[60] *Biochem. Z.*, 1918, **88**, 432; *A.*, i, 423.
[61] *Jahrb. Kinderheilk.*, 1904, **60**, 123. [62] *Ann. Reports*, 1920, **17**, 161.
[63] Greenwald, *J. Biol. Chem.*, 1916, **25**, 431.
[64] Bloor, *ibid.*, 1918, **36**, 49.
[65] Howland and Kramer, *Amer. J. Dis. Child.*, 1921, **22**, 105; *A.*, i, 418.
[66] *J. Amer. Med. Ass.*, 1923, **79**, 2210; *A.*, i, 624.
[67] Kramer and Boone, *Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 87.
[68] Steenbock, Hart, Jones, and Black, *J. Biol. Chem.*, 1923, **58**, 59.

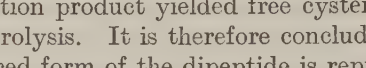
in rickets, J. H. Clark [69] records that the exposure of blood-serum to ultra-violet radiation increases the amount of dialysable calcium.

Biological Oxidations.

The gradual revelation step by step of the significance of glutathione [70] in relation to the mechanism of oxidations in living tissues becomes more fascinating with each publication from the laboratories of Hopkins and his colleagues. Hope was expressed by the reporter last year that the constitution of the dipeptide would soon be established, and by the careful work of Quastel, Stewart, and Tunnicliffe [71] that has now been done. Working with rather less than 2 grams of material, and employing the method of condensation with 2 : 3 : 4-trinitrotoluene used so successfully by Barger and Tutin [72] to determine the constitution of carnosine, these workers found that the condensation product yielded free cysteine but no free glutamic acid on hydrolysis. It is therefore concluded that the constitution of the reduced form of the dipeptide is represented either by I or II.

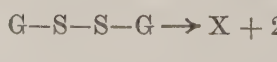


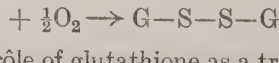
(I.)



(II.)

On oxidation of glutathione with hydrogen peroxide in the presence of a trace of iron salt no trace of succinic acid was detected, whereas after hydrolysis of the oxidation product a yield of succinic acid amounting to 50 per cent. of the theoretical was obtained. From Dakin's studies on the oxidation of α-amino-acids [73] this would indicate that formula II represents glutathione. In last year's Report, attention was directed to the remarkable discovery of a thermostable component of washed tissues which together with glutathione can form a system capable of absorbing atmospheric oxygen. The mechanism of this change may be represented by the following scheme, in which X stands for the as yet unidentified tissue constituent, and G—S—S—G and G—SH for the oxidised and reduced forms of glutathione, respectively.





This characteristic rôle of glutathione as a transporter of hydrogen will cease, of course, when the supply of the oxidisable component

[69] *Amer. J. Hyg.*, 1923, **3**, 4, 81. [70] *Ann. Reports*, 1921, 1922.
[71] *Biochem. J.*, 1923, **17**, 586; *A.*, i, 1072.
[72] *Ibid.*, 1918, **12**, 402; *A.*, i, 170.
[73] *J. Biol. Chem.*, 1905, **1**, 111; **5**, 410; *A.*, 1906, ii, 105.

is exhausted. Naturally, there has been keen interest focussed on the possible nature of the tissue component, but as yet no definite information on this point is available. A clue may, however, have been provided by the experiments of both Meyerhof and Hopkins on the autoxidation of unsaturated fatty acids under the influence of glutathione and similar substances. Meyerhof [74] has found that washed frog's muscle, which regains the power to absorb oxygen in the presence of substances containing the sulphydryl group –SH, such as thioglycollic acid or cysteine, may be replaced by the material precipitated by acetone from the alcohol–ether extract of the muscle-tissue. This at once suggests substances of the lecithin class, and a reduction in the amount of unsaturated groupings present during the process further suggests that unsaturated fatty acids (linolenic) may be concerned. Strong support for this idea is furnished by his experiments with lecithin and by the work from the Cambridge laboratory.[75]

When the system outlined in the scheme given above ceases to absorb oxygen, it is because all the tissue constituent X has been oxidised. If, however, an emulsion of an oil containing unsaturated fatty acids (linseed or cod-liver oil) be part of the system, there is a greatly increased uptake of oxygen, and, generally speaking, the increase is proportional to the amount of fat added. Control tests on the emulsion, alone or mixed with the tissue residue, show that it takes up oxygen at a very much slower rate. If, however, the oil emulsion be mixed with the dipeptide, there will be a marked oxidation of the former provided the reduced form of the catalyst is present. This condition is essential because the oil has no power to reduce the disulphide form such as is possessed by the tissue component X.

In these circumstances, glutathione acts as an agent for oxygen transport, probably, as both Meyerhof and Hopkins think, by the intermediate formation of an unstable peroxide. This reaction may perhaps be illustrated by such a scheme as :

$$\begin{matrix} G{-}SH \\ G{-}SH \end{matrix} \xrightarrow{O_2} \begin{matrix} G{-}S{-}H \\ G{-}S{-}H \end{matrix}\!\!\begin{matrix} O \\ O \end{matrix} \xrightarrow{M} \begin{matrix} G{-}SH \\ G{-}SH \end{matrix} + MO_2$$

The liberated oxygen will be taken up presumably at the unsaturated linking of the fatty acids (M) present in the oil. On the other hand, if the tissue component X is present, the oxidation of the oil will proceed without the necessity of the reduced form of glutathione being present, for it possesses the necessary power

[74] *Pflüger's Archiv*, 1923, **199**, 531; *A.*, 1924, i, 118.
[75] Hopkins, *Lancet*, 1923, i, 1251.

itself to reduce the disulphide compound. It is for this reason that in the absence of the tissue component the oxidation of unsaturated fatty acids by the agency of glutathione ceases as soon as the dipeptide is converted wholly into the disulphide form, but proceeds fully when the presence of the tissue components enables the necessary reduction of the disulphide to occur. As Hopkins has remarked, "We see, then, that the oxidation of a substance involving one type of change (let us say hydrogen transport) may control the oxidation of another substance involving another type of change (oxygen transport); we may recognise here an indication of that correlation and organisation of chemical events which is so characteristic of living tissues."

Dixon and Tunnicliffe [76] have carefully examined the reduction of methylene-blue by the sulphydryl grouping in glutathione, cysteine, and thioglycollic acid and show, as Strassner [77] showed for the last-named substance, that the reaction curve resembles that of an autocatalytic reduction.

The active agent causing the catalysis is the disulphide form produced by the reaction, and they present some evidence that a more active intermediate compound of the R—SH with the R—S—R—S compounds may be formed. The reduction potentials of cysteine and of glutathione are, however, independent of the presence or absence of their oxidised forms.[78] The uptake of oxygen by the sulphydryl grouping of cysteine [79, 80] and glutathione [76] is most rapid at p_H 7·4, a fact which is obviously of considerable significance from the physiological point of view. These results naturally lead us to consider the glutathione system in the light of the views on oxidation which are associated to a large extent with the names of Warburg and Meyerhof. The development of these views is traced in a most illuminating manner by Meyerhof himself in a lecture which he has recently given.[81] The essential points of their beliefs are that oxidation *in vivo* is closely associated with actual structures present in the cell, and that the occurrence of oxidation at the surface of these structures is to a considerable extent dependent on the presence of iron. Indeed Warburg conceives the surface of such structures as a mosaic of areas containing iron and of others free from iron.

Such a conception satisfies experimental results obtained in

[76] *Proc. Roy. Soc.*, 1922—23, [*B*], **94**, 266; *A.*, i, 416.
[77] *A.*, 1911, ii, 57.
[78] Dixon and Quastel, *T.*, 1923, **123**, 2943.
[79] Mathews and Walker, *J. Biol. Chem.*, 1909, **6**, 289; *A.*, 1909, i, 289.
[80] Abderhalden and Wertheimer, *Pflüger's Archiv*, 1923, **197**, 131; *A.*, 1924, ii, 11.
[81] *Lancet*, 1923, i, 322.

studying the inhibition of oxidation by narcotics or by cyanides, whether in the living cells, or in simpler systems such as blood charcoal suspended in aqueous solutions. In general, narcotics depress oxidation in proportion to the degree to which, by surface tension, they replace the substrate on the surface of the structure, whereas, in the case of cyanides, in which no relation can be traced between their very powerful inhibitive effect on oxidation and the extent to which they are adsorbed by the surfaces, it is believed that by chemical interaction the iron-containing areas are inactivated.[82, 83]

Certainly these views are strongly supported by Warburg's experiments on the oxidation of cystine at charcoal surfaces.[84]

Meyerhof [85] has now suggested that the inhibitive effect of hydrocyanic acid on the autoxidation which occurs in the presence of substances containing the sulphydryl group is due to the inactivation of traces of metals, and he has been able to show that the autoxidation of thioglycollic acid in presence of traces of copper may be inhibited by the formation of complex compounds of copper and cyanogen when cyanides are present.

This is not in agreement with the conclusions of Abderhalden and Wertheimer,[86] who found that oxidation of cysteine takes place in the absence of iron, although its presence accelerates the change. Furthermore, these authors state that cyanides depress the oxidation in the absence of iron. It is probable, however, in considering the system formed by glutathione in conjunction with the heat-stable preparation from washed muscle that some progress will be achieved by testing the application of the views of Warburg.

In the light of the now popular idea that sugars before oxidation or metabolism are converted into compounds with phosphoric acid, it is interesting to note that Meyerhof and Weber [87] have ascertained that dextrose is not appreciably oxidised at the surface of blood charcoal suspended in an aqueous solution of the sugar, but that hexosephosphate is slowly but surely changed. Fructose was unaffected, and lactic acid only very slightly oxidised. The oxidation of amino-acids under similar conditions [88] has been examined by Ellinger and Landsberger,[89] who in general agree with Warburg's main ideas. Baur [90] has found that glycine in aqueous

[82] *Naturwiss.*, 1923, **11**, 159.
[83] *Biochem. Z.*, 1923, **136**, 266; *A.*, i, 501.
[84] *Ibid.*, 1921, **119**, 134; *Pflüger's Archiv*, 1923, **200**, 203.
[85] *Pflüger's Archiv*, 1923, **200**, 1.
[86] *Ibid.*, 1923, **198**, 122; *A.*, 1924, i, 11.
[87] *Biochem. Z.*, 1923, **135**, 558; *A.*, ii, 317.
[88] Warburg, *A.*, 1921, i, 230; 1922, i, 190.
[89] *Z. physiol. Chem.*, 1922, **123**, 246, 264; *A.*, i, 73.
[90] *Helv. Chim. Acta*, 1922, **5**, 825; *A.*, i, 97.

solution is hydrolysed at the surface of charcoal in the absence of air. The reaction probably occurs according to the equation

$$NH_2{\cdot}CH_2{\cdot}CO_2H + H_2O \longrightarrow OH{\cdot}CH_2{\cdot}CO_2NH_4,$$

but attempts to separate glycollic acid were unsuccessful.

The hypothesis advanced by Hopkins (p. 191) that glutathione may act as an oxygen transporter by the intermediate formation of a loose type of peroxide recalls the generally accepted conceptions of the so-called "oxidase" system as propounded by Bach and Chodat in 1903. These were that there is a substance, probably an enzyme (oxygenase), which can unite with molecular oxygen to form a peroxide, which is then broken down by the action of a second enzyme (peroxydase) with the liberation of *active* oxygen. If Hopkins is justified in his speculation, it is possible to view glutathione as an oxygenase, but as one which is not an enzyme and which does not need the co-operation of a peroxydase to effect oxygen transport. Gallagher [91] has examined the mechanism of oxidation in plants, and has shown that there is no definite evidence that the substances, oxygenases, which form intermediate peroxides in plant juices exposed to air are enzymes, as Bach and Chodat held, and that it appears that they are autoxidisable substances. A substance of this nature isolated from fresh potato tubers was found to bear a close relation to the lipins. The view expressed by Onslow [92] that the constituents of plant juices which form organic peroxides are of the nature of catechol is not supported, and it is shown that the darkening of such juices is due to the action of tyrosinase on tyrosine. It is very encouraging to catch a glimpse already of the manner in which one day the new theories concerning oxidation in the tissues may be linked up with the older theories in which peroxides formed so important a part, and which still rest on the sound foundation of Dakin's classic work.[93]

The Chemistry of Muscular Contraction.

Although Professor Barger reviewed this subject in the *Annual Reports* for 1921, it is obvious from a perusal of the literature that many important advances have been made during the intervening years. It must be said, however, that most of the new facts are concerned with the thermodynamical aspect of the problem, rather than with purely chemical matter, in which field there is not much new to report.

The general position of our knowledge of this subject has recently

[91] *Biochem. J.*, 1923, **17**, 515; *A.*, i, 1159.

[92] *Ibid.*, 1919, **13**, 1; 1920, **14**, 535.

[93] "Oxidation and Reduction in the Animal Body," 2nd edn., London, 1922.

been made clear by a valuable summary by Hill and Meyerhof.[94] Both experiments on isolated muscle and on man have proved that the production of lactic acid in muscle contraction is very sudden. Thus, violent exercise lasting only ten seconds may produce in an athlete an oxygen "debt" corresponding to the oxidative removal of no fewer than 30 grams of lactic acid, or 0·1 per cent. of the active muscles.[95] Obviously the sudden liberation of so much acid is a serious call on the neutrality-regulating mechanism of the body, and there has been considerable speculation as to the nature of the means employed to readjust promptly the normal reaction of the tissues. Meyerhof[96] has shown that the available salts, bicarbonate, and phosphates could not under the conditions possibly furnish the necessary basic radicals, and has suggested that the muscle possesses in certain of its colloidal constituents large reserves of far more effective buffers than the alkaline salts of the tissue fluids. Hartree and Hill have recently shown[97] that this hypothesis may actually provide a closer agreement between the observed heat liberated during contraction and relaxation, and the calculated value, since it provides for a greater heat of neutralisation of the lactic acid produced. In this paper further evidence is brought forward to show that the proteins of blood, in particular the sodium or potassium salt of hæmoglobin, may act as effective buffers in preventing a marked rise of hydrogen-ion concentration. Probably the proteins of the plasma can also act in this capacity, but to a much less extent, as Milroy has shown,[97a] in opposition to the view held by Bayliss.[98] The isolation from living muscle of an alkaline protein buffer capable of functionating in such an efficient manner when lactic acid is produced will be awaited with interest.

Hartree and Hill give in their paper the following "balance sheet," which represents a summary up to date of their views regarding the distribution of heat production in the various phases of the cycle of the isometric contraction of frog's muscle.

Phase.	Relative.	Absolute, per gram of lactic acid.
Total anaërobic	1·25	370
Total initial	1·0	296
Total delayed anaërobic	0·25	74
Total oxidative	2·5	740
Initial (contraction)	0·6	178
Initial (relaxation)	0·4	118
Oxidative delayed	1·5	444

[94] *Ergeb. Physiol.*, 1923, **22**, 300.
[95] Hill and Lupton, *Quart. J. Med.*, 1923, 135; *A.*, i, 977.
[96] *Pflüger's Archiv*, 1922, **195**, 22; *A.*, i, 268.
[97] *J. Physiol.*, 1923, **58**, 125. [97a] *Ibid.*, 1923, **57**, 253.
[98] *Ibid.*, 1919, **53**, 162.

The initial anaërobic heat can, as Slater [99] has just shown, be satisfactorily accounted for by the production of lactic acid from glycogen. Employing the accepted value for the heat of combustion of glycogen,[1] it appeared that the calculated heat given out by the production of one gram of lactic acid from glycogen, and the subsequent neutralisation by the alkaline salt of a protein, would account for the initial heat, but leave the delayed anaërobic heat entirely unaccounted for. This, and other considerations, led to a redetermination of the heat of combustion of glycogen, with the result that Stohmann and Schmidt's value has been replaced by the value of 3874 cals. per gram for the hydrated product $(C_6H_{10}O_5,H_2O)_n$. This value is nearly 100 cals. higher than that previously accepted. Slater concludes, on the basis of the following scheme, that it is possible, using this new figure, to explain the actual heat measurements on muscle entirely on chemical grounds.

Contraction. (*a*) Glycogen $\longrightarrow$ lactic acid.
(*b*) Lactic acid and contractile mechanism produce mechanical response.

Relaxation. (*a*) Lactic acid + $\begin{matrix}Na_2HPO_4\\NaHCO_3\end{matrix}$ $\longrightarrow$ Na lactate + $\begin{matrix}NaH_2PO_4\\H_2CO_3\end{matrix}$

Anaërobic recovery. (*a*) $\begin{matrix}NaH_2PO_4\\H_2CO_3\end{matrix}$ + Na protein $\longrightarrow$ H protein + $\begin{matrix}Na_2HPO_4\\NaHCO_3\end{matrix}$

Previously Hartree and Hill had directed attention to their inability to account satisfactorily for the delayed anaërobic heat produced. This heat appears to be about 0·25 of the initial heat, and its rate of evolution is unaffected by temperature. In accordance with the above scheme, Slater has produced evidence that it may represent the replacement of the intermediate and temporary buffering of the lactic acid with bicarbonate and disodium phosphate by the more efficient buffering with proteins. Such a complete change would require a further 119 cals., and as only 74 are actually evolved it is assumed that the change proceeds only to about 60 per cent. completion. The independence of this heat production on temperature is explained by Slater on the grounds that the controlling factor in the velocity of reaction is the physical one of the rate of diffusion of the acid phosphate and carbonic acid ions through the muscle-tissue.

From the figures which Hartree and Hill have advanced it is apparent that between 1 part in 4·7 parts and 1 part in 6 parts of the lactic acid removed is oxidised, the remainder being retained as glycogen. Hill, Long, and Lupton,[2] using the retention of carbon dioxide as a measure of lactic acid removal, and the oxygen

[99] *J. Physiol.*, 1923, **57**, 163.
[1] Stohmann and Schmidt, *J. pr. Chem.*, 1894, [ii], **50**, 385.
[2] *Proc. Physiol. Soc.*; *J. Physiol.*, 1923, **57**, xiv.

used in recovery as a measure of the lactic acid oxidised, found the ratio between lactic acid removed and lactic acid oxidised after exercise in man to be 4·2; a value much the same as that given by experiments on frog's muscle. In later experiments, in which the lactic acid was determined directly instead of by the indirect method of determining the retention of carbon dioxide, Long and Lupton [3] obtained values ranging from 4·96 to 9·10 with a mean of 7·5. From these values they regard the efficiency of removal as being greater in man than in the case of the frog's muscle, but too much significance cannot be placed on these differences. Lesser [4] states, however, that the observations of Meyerhof [5] on the disappearance of glycogen from, and the formation of lactic acid in, exercised muscle cannot be applied to the whole animal. Lesser finds, in contrast to Meyerhof's records, that in the winter, during anoxybiosis, 40 per cent. of the total loss of glycogen in frogs occurs in the liver, whereas in summer under the same conditions only 15 per cent. is so lost. During restitution, the resynthesis of glycogen in the muscle is independent of the season, but during winter it is in part masked by the concurrent diminution of liver glycogen.

As remarked above, the past year's work does not record any important advance in the purely chemical study of intermediate carbohydrate metabolism in the muscle. Laquer and Meyer [6] find that fresh frog's muscle produces lactic acid more readily from glycogen than from a number of other carbohydrates tested; lævulose, starch, dextrose, and mannose follow in order of decreasing lactic acid yield, whilst no acid was produced from galactose, sorbose, sucrose, maltose, diamylose, tetra-amylose, and inulin. The mechanism by which part of the lactic acid is oxidised during the recovery process is still obscure, but Hirsch [7] claims to have detected acetaldehyde as an intermediate product.

Not unrelated to the production of lactic acid from carbohydrate in muscle are the observations recorded by Anrep and Cannan [8] on the concentrations of lactic acid in the blood in experimental alkalæmia and acidæmia. It will be remembered that Macleod and his collaborators [9] showed that administration of alkali may cause an increase of lactic acid in the blood and urine, an increase of glycolysis in blood, and a decrease in blood-sugar concentration.

[3] *Proc. Physiol. Soc., J. Physiol.*, 1923, **57**, lxvii.
[4] *Biochem. Z.*, 1923, **140**, 577; *A.*, i, 1154.
[5] *Pflüger's Archiv*, 1920, **185**, 20.
[6] *Z. physiol. Chem.*, 1923, **124**, 211; *A.*, i, 268.
[7] *Biochem. Z.*, 1922, **134**, 415; *A.*, i, 415.
[8] *J. Physiol.*, 1923, **58**, 244.
[9] *Amer. J. Physiol.*, 1917, **42**, 193, 460; 1918, **47**, 189.

Moreover, Macleod [10] also recorded some experiments on lactic acid in anoxæmia. As Anrep and Cannan point out, the interpretation of the results is complicated by the fact that in these experiments the anoxæmia was accompanied by a lack of carbon dioxide. Employing a technique providing adequate control on this point, Anrep and Cannan report that the concentration of lactic acid rises when the alkalinity of the blood is increased, and falls again when the reaction moves towards acidity. The concentration of lactic acid in the blood would seem to be primarily dependent on the reaction of the blood rather than on the tension of oxygen or carbon dioxide. The mechanism of the removal of lactic acid from the blood, and in part also its appearance in the blood, is resident in the tissues. The authors view this mechanism as another line of defence by which the organism can protect itself against excessive changes in the reaction of the blood.

Specific Bacterial Substances.

Some few years ago it was shown by Dochez and Avery [11] that a substance is present in cultures of pneumococci grown in fluid media which precipitates specifically in anti-pneumococcus serum of the homologous type.

The presence of this soluble substance is best demonstrated during the initial period of rapid growth of the organisms in culture, and can also be detected in the blood and urine both of experimentally infected animals and of human patients suffering from lobar pneumonia. The substance is not destroyed by boiling. It is readily precipitated from aqueous solution by acetone, alcohol, ether, or colloidal iron, and does not pass through a dialysing membrane, whilst the serological reactions are not affected by digestion by trypsin. Naturally, the authors regarded such a substance as an ideal starting point for a study of the relation between bacterial specificity and chemical constitution. Recently Zinsser and Parker [12] have described the preparation from filtered alkaline extracts of various pulverised bacteria, amongst them pneumococci, of substances which appear to be free from coagulable protein, which they term "residual antigens." These substances show specific precipitation with homologous antisera, and are regarded by their discoverers as being related to the substance described by Dochez and Avery. Zinsser and Parker were, however, unable to produce anti-bodies by injecting their "residual antigens" into animals. Heidelberger and Avery [13] now describe the preparation of the specific substance from cultures of pneumo-

[10] *Amer. J. Physiol.*, 1921, **55**, 184.
[11] *J. Exper. Med.*, 1917, **26**, 477.
[12] *Ibid.*, 1923, **37**, 275.
[13] *Ibid.*, 1922, **38**, 73.

cocci, and a method by which the crude material may be considerably purified so as to concentrate its specific properties. By the method outlined, it is possible to obtain about 1 gram of material from 75 litres of broth culture, and the preparation is a colourless, varnish-like mass.

As remarked before, this product is unaffected by heating at 100°. Furthermore the method of preparation eliminates all substances precipitable by phosphotungstic acid or giving a biuret test. No claim is made that the final product is a chemical entity, but the remarkably interesting fact is established that it consists very largely of a polysaccharide yielding glucose on hydrolysis. Whilst our general knowledge of the properties of "active principles" naturally leads us to think of such a product as an "adsorption complex," the fact that its specific activity increases as purification raises the carbohydrate content of the material suggests that the polysaccharide may actually be the soluble specific substance. Attempts to stimulate anti-body production by the immunisation of animals with the purified substance yielded negative results. It is interesting to note that this substance is chemically analogous to the bacterial "gum" described by other investigators,[14] and which is apparently derived from the capsule. In a later paper, Avery and Heidelberger [15] present evidence that in the cell of pneumococcus there may be at least two distinct substances which are intimately concerned with its biologic specificity. One of these is the specific soluble substance described above, whilst the second is a protein fraction which they have isolated by precipitation from extracts of pneumococci by acetic acid. This material appears to consist of nucleoprotein and mucoid, and to exhibit species specificity rather than the type specificity shown by the carbohydrate preparation.

J. C. Drummond.

[14] Kramár, *Centr. Bakt.*, 1922, **87**, 401, and earlier literature.
[15] *J. Exper. Med.*, 1923, **38**, 81.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

In this Report the general arrangement of subject matter is the same as that adopted last year, following the more or less logical sequence of: the soil and soil phenonema *per se*; the influence of soil and related factors on plant growth; the biochemistry of the living plant; the constituents of the plant.

Unfortunately, the amount of material calling for comment under these headings has proved to be so large that it has not been possible this year to devote any space to enzyme action and the biochemistry of micro-organisms (apart from soil micro-organisms). A discussion of the very considerable amount of work which has been carried out in these fields of the subject during the past year or two would swell this Report to prohibitive dimensions. In any case, the subject is at present developing rapidly, and it is better to defer for another year a critical discussion of the position, by which time it will probably be easier to pick out the main advances from the large mass of experimental facts.

As in former years, this Report should be read in conjunction with that to the Society of Chemical Industry on "Soils and Fertilisers." In the latter Report an attempt has been made to deal with all the more technical aspects of the subject, including the chemistry, analysis, and agricultural applications of fertilisers, and laboratory methods for the examination and analysis of soils, leaving for this Report a consideration of the more theoretical aspects of the subject.

The Soil.

Soil Colloids.

Modern work on soils is tending more and more to take special account of the colloidal matter in soils and its influence on their properties.

The weathering of minerals and the chemical denudation of soils have hitherto been considered almost entirely from the point of view of the removal of the products of weathering in true solution, and the accumulation of insoluble colloidal alumino-silicates in the residue. Whitney,[1] however, has pointed out the possibility that chemical erosion is not a selective process, that is to say, that in the breaking down of silicates to a point at which, say, potassium

[1] M. Whitney, *Science*, 1922, **56**, 216; *A.*, i, 80.

goes into true solution, silica, alumina, and iron may also go into colloidal solution in the same proportion as they bear to the potassium content of the original material. Further investigations will be necessary to decide this point. The amount of potassium brought into solution from finely ground (200-mesh) orthoclase by water treatment was found by Haley [2] to be considerable; the potash so dissolved was readily available to buckwheat plants in sand cultures.

The constitution of the inorganic colloids, known as the clay or the "colloidal clay," in the soil has been a subject of considerable speculation. The view was formerly held that zeolites existed in the soil, but for lack of satisfactory evidence this idea is now generally discounted, although it still crops up from time to time, as in the case of a paper by Scurti,[3] who seeks to explain certain soil properties in terms of the properties of the natural zeolites. Although the existence in the soil of actual zeolites as such has not been proved, recent work shows quite clearly that in such phenomena as absorption and basic exchange there is evidence for the existence in the soil of colloids with reactive acidic groupings, which may be regarded as analogous to zeolites in many ways. This aspect of the subject is discussed more fully on pp. 204–207.

The colloidal material extracted from a heavy clay soil has been examined by Bradfield.[4] The analyses of the material indicated that the natural colloid might be composed of the completely broken down products of weathering, that is, colloidal silica, alumina, and ferric hydroxide, but on comparison of the natural colloid with a synthetic mixture of these three colloidal materials, it was found that the two behaved quite differently with regard to cataphoresis, buffer action, and towards electrolytes. The inorganic colloid of the soil evidently consists mainly of a complex, readily decomposable alumino-silicate.

The effect of the soil colloids on the physical properties of the soil is well illustrated by the work of Haines [5] and of Hardy [6] on the shrinkage of soils on drying. The latter worker interprets his results on the assumption that the colloidal gel coating around the soil particles possesses a reticulate structure; at the point of saturation the hydrogel contains water in two phases, one of water absorbed in the walls of the gel and the other filling the vesicles of the gel.[7] The shrinkage of soils and clays on drying is supposed to be due

[2] D. E. Haley, *Soil Sci.*, 1923, **15**, 167; *A.*, i, 888.
[3] F. Scurti, *Ann. Chim. Appl.*, 1923, **13**, 161; *A.*, i, 1047.
[4] R. Bradfield, *Missouri Agr. Exp. Sta. Research Bulletin*, 60, 1923.
[5] W. B. Haines, *J. Agric. Sci.*, 1923, **13**, 296. [6] F. Hardy, *ibid.*, p. 243.
[7] See also Wilsdon, *Mem. Dept. Agri. India, Chem. Ser.*, 1921, **6**, 3, who has advanced similar views with regard to the structure of the colloidal material in the soil.

solely to loss of vesicular water. Hardy has also applied the same hypothesis to a study of the maximum water-retaining capacity and certain other soil moisture constants.[8] He urges the importance of recognising the specificity of soil colloidal material, as illustrated by the marked difference in physical behaviour between clay soils containing hydrophilous siliceous colloids which swell greatly when wetted, and lateritic soils the colloid of which consists mainly of alumina and ferric oxide hydrogels, which do not exhibit marked swelling on wetting.

E. A. Fisher has published some interesting and suggestive papers on the evaporation of water from soil, clay, and other materials.[9] Using the elegant experimental method originally devised by Keen,[10] he has studied the characteristic curvature which is exhibited by the curve for the rate of evaporation of moisture from soils. This curvature was ascribed by Keen, and by Fisher in his earlier papers, to the shrinkage of the colloid as it dried, with a resultant diminution of evaporating surface. It has now been found, however, that ball clay, which also exhibits shrinkage on drying, does not give an evaporation curve with the characteristic curvature shown by that for soil, and it is concluded that this particular type of curvature is characteristic of the evaporation curves of such materials as soil which are mixtures of colloidal and non-colloidal substances, and that it is due to the simultaneous evaporation of imbibitional water held by the colloid and of interstitial water wedges between the soil grains. The former water evaporates at a practically constant rate, whilst the latter evaporates at a rapidly diminishing rate, curvature in the evaporation curve resulting. Fisher's " imbibitional " water evidently corresponds to what is termed " vesicular " water by Wilsdon and Hardy.

The flocculation of colloidal clay has been studied by Bradfield,[11] who finds that flocculation is brought about by many common acids at about the same hydrogen-ion concentration.

The absorption of electrolytes by soils and the part played by the soil colloids in this process are being extensively studied in the Bureau of Soils of the U.S. Department of Agriculture. It has been shown that, except for the most highly micaceous soils, in which the non-colloidal absorption might reach 10—20 per cent. of the whole soil absorption, less than 5 per cent. of the total absorption of the soil is due to the non-colloidal part.[12] Absorption by non-

[8] F. Hardy, *J. Agric. Sci.*, 1923, **13**, 340.

[9] E. A. Fisher, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 139, 664; *J. Agric. Sci.*, 1923, **13**, 121.

[10] B. A. Keen, *J. Agric. Sci.*, 1914, **6**, 456.

[11] R. Bradfield, *J. Amer. Chem. Soc.*, 1923, **45**, 1243; *A.*, ii, 470.

[12] M. S. Anderson, W. H. Fry, P. L. Gile, H. E. Middleton, and W. O. Robinson, *U.S. Dept. Agr. Bull.*, 1922, **1122**, 1—20; *A.*, i, 283.

colloidal constituents should therefore not seriously affect absorption methods for estimating the amount of colloids in soil. In the same laboratory, the absorption of electrolytes by silica, alumina, and ferric hydroxide gels is being studied with regard to their bearing on the properties of soils,[13] but in view of the results of Bradfield (see p. 201) it is evident that the application of the results to the interpretation of soil phenomena must be carried out with caution.

The absorption of phosphates by the soil probably depends on somewhat different factors from those governing the absorption of bases. Fraps [14] has studied the influence of various factors on the process. His results appear to indicate that iron and aluminium oxides have a more important effect than lime on the fixation. The organic matter of the soil is also of importance. Auten [15] has found considerable amounts of phosphorus in the soil in organic combination, not in the form of nucleic acid, phytin, lecithin, or pyrimidine nucleotides, but apparently in an amphoteric organic complex, in combination with calcium and magnesium, or other bases.

The chemical properties of the inorganic colloids of the soil have an important bearing on the phenomena of absorption, basic exchange, and acidity in soils. The colloidal coating on the surface of the mineral soil particles must be supposed to consist largely of a gel composed of complex aluminosilicic acids, containing reactive acid groupings which are saturated to a greater or less degree by bases. Some time ago Gans (now known as Ganssen) put forward the hypothesis that it was possible to deduce, from the molecular proportion of silica, alumina, and bases in the colloidal clay of the soil, the solubility of the nutrient materials in, and the manurial needs of the soil. According to his view, if the molecular ratio $SiO_2 : Al_2O_3$: bases (CaO, MgO, K_2O, Na_2O) is 3 or more : 1 : 1, the soil is absorptively saturated or neutral, an active exchange of the bases takes place between the salts in the soil solution and the colloidal clay, and the soil is fertile. If, however, the ratio is 3 or more : 1 : less than 1, the soil is acid and the salts in the soil solution are decomposed with absorption of the kation; and the soil is no longer fertile.[16] A number of heavy clay soils have been investigated from this point of view by Tacke and Arnd,[17] who found that

[13] R. C. Wiley and N. E. Gordon, *Soil Sci.*, 1922, **14**, 441; *A.*, i, 524; E. B. Starkey and N. E. Gordon, *ibid.*, 449; *A.*, i, 523; D. C. Lichtenwalner, A. L. Flenner, and N. E. Gordon, *ibid.*, 1923, **15**, 157; *A.*, i, 888.

[14] G. S. Fraps, *Texas Agr. Expt. Sta. Bull.*, 1922, No. 304; *A.*, i, 1167 See also G. Leoncini and F. A. Rogai, *Agr. Italiana*, 1922, **45**, Nos. 4—6, 109; *A.*, i, 1167.

[15] J. T. Auten, *Soil Sci.*, 1923, **16**, 281; *A.*, i, 176.

[16] See R. Ganssen (Gans), *Z. Pflanz. Düng*, 1923, II, *A*, 370, where references to his earlier papers are also given.

[17] B. Tacke and T. Arnd, *Internat. Mitt. Bodenkunde*, 1923, **13**, 6.

the known manurial needs of these soils could not be correlated with the molecular ratio of $SiO_2 : Al_2O_3$: bases in the above manner.

We can, however, leave the question of the molecular composition of the alumino-silicic complex for the time being, and pass on to a consideration of the chemical properties of that complex as a whole. The affinity for kations which finds expression in the phenomena of soil acidity, basic exchange, and absorption may be regarded as a chemical affinity due to acidic groupings in the colloid. It is possible from this point of view to interpret most of the above phenomena on the basis of chemical reactions under stoicheiometrical relationships and subject to the laws of mass action, due regard being paid to the implications of the fact that one of the reactive ions forms part of a colloidal phase, which is thus akin to a colloidal electrolyte. There is, in fact, in modern views a swinging back towards the ideas of the presence in soils of reactive silicates, as originally advanced by Way,[18] with the important difference that the colloidal nature of those silicates is also taken into account. This may perhaps be regarded as a logical outcome of modern views as to the nature of the forces involved in interfacial phenomena; improved knowledge of the nature of molecular forces is tending to sweep away the older ideas as to the sharpness of the distinction between so-called physical adsorptions and chemical reactions.

Bradfield [19] has found that the same amount of a suspension of an acid colloidal clay was required to neutralise equivalent quantities of calcium or sodium hydroxide, using electrometric and conductometric methods of determining the end-point. The conductivity curves, which were of the type usually obtained in titrating a strong base with a weak acid, exhibited definite breaks, indicating the neutralisation of definite acids, which in 1 per cent. solutions had concentrations ranging, for four different clays, from 0·0027 to 0·0037*N*. It is therefore concluded that the reaction between acid colloidal clays and strong bases is an ordinary neutralisation and that recourse to a theory of (physical) adsorption is unnecessary.

It is now definitely established that, when a soil is treated with a solution of a neutral salt, the interchange of kations between the solution and the reactive colloids of the soil takes place according to stoicheiometric laws, so that the amount of the kation of the neutral salt that disappears from the solution is chemically equivalent to the amount of the kations that leave the colloid and appear in the solution. Moreover, the amount of the absorbed * ion, and of

[18] J. T. Way, *J. Roy. Agric. Soc. Eng.*, 1850, **11**, 313; 1852, **13**, 123.

[19] R. Bradfield, *J. Amer. Chem. Soc.*, 1923, **45**, 2669.

* The word "absorbed" is used here and in the following discussion merely as a convenient method of referring to the bases held by the soil colloids in the fashion indicated above.

the replaced ions, at equilibrium, is an exponential function of the equilibrium concentration of the replacing ion in the solution, these reactions conforming to the general type of Freundlich's absorption curves and equations. If, however, the soil is continually treated with fresh portions of the original neutral salt solution, the equilibrium is continually disturbed, and ultimately the whole of the originally absorbed kations will be removed from the soil. This forms the basis of the method developed by Hissink [20] for the determination of the replaceable bases in the soil, which seems likely to prove of considerable value in the study of the fertility and fertiliser requirements of soils.

It is obvious from the above relationships that when the soil is treated with a solution of a neutral salt, the soil colloids undergo a change which is reciprocal to that of the solution. Thus when the original concentration of the neutral salt solution is greater than that which would be in equilibrium with the kations absorbed by the soil colloids, the decrease in concentration of the kation of the neutral salt in the solution is accompanied by an increase in the concentration of that kation in the colloidal phase. When the reaction is carried to an end by continual treatment with the original salt solution, the colloidal phase will then be saturated with the kations of the neutral salt. By the application of these views to the special case of the action of sodium salts on soils, considerable light is thrown on the genesis of sodium carbonate in " alkali " soils, and on the processes operative in the conversion of a saline soil into an " alkali " soil. In a normal fertile soil containing a sufficiency of lime, the colloidal phase contains a large proportion of calcium-ions, and the resulting complex appears to be a stable gel. On treatment with sodium salts, the absorbed calcium is replaced to a great extent by sodium. In the presence of excess of sodium salts, this sodium–clay complex is stable, but on removal of the excess of sodium salts by washing, the sodium–clay complex readily hydrolyses with the production of sodium hydroxide, which is rapidly converted into sodium carbonate by the carbon dioxide in the soil atmosphere. Although work somewhat along these lines was carried out in France as long ago as 1888 by Mondésir,[21] priority in the detailed development of these views must be given to Gedroiz, whose work has been rather overlooked by most soil investigators owing to its having been published only in Russian.[22] Later, Dominicis,[23] Prescott,[23a] and

[20] See *Ann. Rep. Appl. Chem.* (*Soc. Chem. Ind.*), 1921, **6**, 415; also *Soil Sci.*, 1923, **15**, 269; *A.*, i, 992.

[21] P. de Mondésir, *Compt. rend.*, 1888, **160**. 459.

[22] K. K. Gedroiz, *Zhur. Opit. Agron.*, 1912, **13**, 363; 1914, **15**, 181; 1916, **17**, 472.

[23] A. de Dominicis, *Staz. Sper. Agr. Ital.*, 1918, **41**, 103.

[23a] J. A. Prescott, *Cairo Sci. J.*, 1922, **10**, 58.

Hissink [24] put forward very similar ideas, the latter worker having applied them in a suggestive manner to the soil problems arising in the reclamation of land from the sea in Holland. More recently, in California, Cummins and Kelley [25] have made a special study of the formation of sodium carbonate in soils, with special reference to the "black alkali" soils which are of only too common occurrence in that and other parts of the United States. They even succeeded in converting an acid soil into an alkaline one by treatment with sodium chloride followed by washing with water. The position is well summarised by these authors in the following quotation from their paper:

"By essentially chemical processes, probably due to differences in their respective electrolytic solution potentials, sodium has been shown to replace a part of the calcium from the soil silicates readily and rapidly. When the concentration of sodium in solution is high and the calcium set free can be readily removed, a relatively high degree of saturation with sodium may occur. The physical properties of the new sodium silicate combinations are different from those of the original calcium–silicate compounds, and are so pronounced as to alter profoundly the characteristics of the entire soil mass.

"The sodium 'absorbates,' so called, are much less stable than the corresponding calcium compounds. They are probably colloidal in nature, but this has not been established and is not a necessary assumption for an explanation of their behaviour. Their important property is that of slowly hydrolysing in the absence of strong electrolytes. Hydrolytic equilibrium is not rapidly established in nature because the hydroxyl-ions resulting from hydrolysis are readily removed by the CO_2 in the soil atmosphere. This favours the decomposition of the 'absorbates' and the development of alkalinity. Calcium carbonate may also favour the removal of the hydroxyl-ions.

"The other product of the hydrolysis, the silicate complex, shows a tendency to be present in a colloidal state. This, as is well recognised, may be an important factor favouring slow hydrolysis. Furthermore, reactions between the soluble hydrolytic products and the colloid probably favour a high degree of dispersion and account for the marked change in the physical properties of the soil. These striking changes in the physical properties of the soils were always observed associated or coincident with the development of alkalinity, and constitute one of the most important aspects

[24] *Loc. cit.* (20).

[25] A. B. Cummins and W. P. Kelley, *Univ. Calif. Publications, Techn. Paper*, No. 3, 1923. See also W. P. Kelley and E. E. Thomas, *ibid.*, No. 1, 1923; W. P. Kelley and A. B. Cummins, *Soil Sci.*, 1921, **11**, 139.

of the phenomenon. The characteristic hardness and impermeability of many alkaline soils may be ascribed to the presence of sodium 'absorbates,' or the products of their hydrolysis.

"Lessons may be drawn from these studies as to the proper treatment of saline soils. Leaching alone may be expected to lower the concentration of soluble salts, but in some cases, at least, a deterioration of the land may be expected, partly to offset this advantage. In such cases some means must be provided to prevent the hydrolysis of the sodium 'absorbates' with their attendant deflocculation.

"Any means of preventing hydrolysis during and after the removal of the soluble salts, such as the addition of soluble aluminium, ferrous and ferric salts, acids and organic matter, may be expected to be beneficial. There may be some objection to the use of some of these substances, however, since the soil may be left in an unfavourable condition for crop growth. Moreover, none of these materials can correct the fundamental mischief caused by the original sodium salts, *i.e.*, they cannot restore the calcium to its original position in the active soil silicates. The importance of calcium in the silicate-complexes of the soil in maintaining a desirable physical and chemical medium for plant growth can hardly be overemphasised. Soluble calcium salts should not, therefore, be ignored in the practical reclamation of saline lands."[26]

Reference may also be made to a paper by Ssokolowski[27] in which the importance of the replaceable calcium in the colloidal silicates of the soil, and the association of the latter with humic substances, are emphasised; also to an interesting discussion by Hager[28] in which special attention is given to the relative influence of the absorbed calcium- and sodium-ions on the flocculation of soil colloids and the physical condition of the soil.

Soil acidity, in connexion with which so much work has been done in the past few years, may also be regarded in some of its phases as a function of the reactivity of the colloidal silicate complex in the soil, on the lines first developed by Daikuhara[29] and developed by Rice[30] and many subsequent workers.[31] The almost universal presence of soluble compounds of iron and aluminium, and sometimes of manganese, in acid soils is now a generally accepted fact, which forms the basis of the well-known and widely adopted Comber test[32]

[26] In this connexion, see also F. S. Harris, M. D. Thomas, and D. W. Pittman, *J. Agric. Res.*, 1923, **24**, 317.

[27] A. N. Ssokolowski, *Internat. Mitt. Bodenkunde*, 1923, **13**, 81.

[28] G. Hager, *Z. Pflanz. Düng.*, 1923, **2**, *A*, 292; *A.*, i, 1047.

[29] G. Daikuhara, *Bull. Imp. Central Agric. Expt. Sta. Tokio*, 1914, **2**, 1.

[30] F. E. Rice, *J. Physical Chem.*, 1916, **20**, 214.

[31] See *Ann. Rep.*, 1916, **13**, 224; 1918, **15**, 177; 1920, **17**, 178; 1922, **19**, 213.

[32] See *Ann. Rep. Appl. Chem.* (*Soc. Chem. Ind.*), 1923, **8**.

for sour soils. In an acid, or, as Ramann termed it, an " absorptively unsaturated " soil,[33] it may be supposed that the affinities of the reactive groups of the colloidal silicates are only satisfied to a minor extent by absorbed basic ions (for example, Ca''), the bulk of the absorbed ions being those of hydrogen. The exchange which occurs when such a soil is treated with a neutral salt may be supposed to result either in the primary liberation of hydrogen-ions, soluble iron and aluminium salts then appearing as a secondary effect due to the action of the acid on the aluminosilicate, or the iron and aluminium compounds may be liberated actually by direct exchange with the neutral salt.

Until we have a much more precise knowledge of the chemical nature of the reactive silicates in the soil, it is not possible to decide as to the exact mechanism of the reaction. In practice, the important point is the undoubted fact that soluble iron and aluminium compounds occur in acid soils. Most of the investigations on soil acidity, the results of which have been published in the past year, deal with this aspect of the subject; [34] attention may also be directed to Mukherjee's hypothesis regarding the nature of soil acidity,[35] which is somewhat similar to the views formerly put forward by Odén to account for similar phenomena in peat.[36] Willis has studied certain North Carolina soils which are very rich in organic matter (" muck " soils), and is of the opinion that the acidity of these soils is due to nitric acid produced by vigorous nitrification.[37] The influence of soil reaction on plant growth is discussed on p. 218.

The Soil Solution.

Attention was directed in last year's Report [38] to the doubt which exists as to whether it is possible to isolate, from a soil well supplied with colloidal matter, a solution of which the composition really corresponds to that of the soil solution *in situ*. These considerations do not apply so strongly to relatively coarse soils containing little clay. Working on soils of this type and using the Parker displacement method [39] with the addition of positive air pressure on the displacing liquid, Burd and Martin [40] have obtained results confirming the results of Parker, in that successive portions of the displaced fluid were of constant composition and conductivity.

[33] E. Ramann, " Bodenkunde " (Berlin, Parey), 1911, p. 242.

[34] T. Okazawa, *Rikwagaku Kenkyujo Iho*, 1923, **2**, 189; *A.*, ii, 693; P. S. Burgess, *Soil Sci.*, 1923, **15**, 131, 407; *A.*, i, 1047; W. T. McGeorge, *ibid.*, **16**, 195; *A.*, i, 1275; H. Liesegang, *Landw. Vers-Stat.*, 1922, **99**, 191.

[35] J. N. Mukherjee, *Nature*, 1922, **110**, 732; *A.*, i, 79.

[36] S. Odén, *Koll. Chem. Beihefte*, 11, Heft 3—9 (Die Huminsäuren), p. 141.

[37] L. G. Willis, *N. Carolina Agr. Exp. Sta. Technical Bull.*, No. 24, 1923.

[38] *Ann. Rep.*, 1922, **19**, 211.

[39] F. W. Parker, *Soil Sci.*, 1921, **12**, 209; *A.*, i, 914.

[40] J. S. Burd and J. C. Martin, *J. Agric. Sci.*, 1923, **13**, 265.

They also found an inverse proportionality between the total moisture content of the soil and the concentration of the displaced solution as indicated by specific electrical resistance. Moreover, when the solution displaced by water from a given mass of soil was itself used as a displacing agent on another portion of the same soil, the newly displaced solution had the same concentration of electrolytes as the displacing solution. This is taken as showing that the displaced solution corresponds in composition to the soil solution *in situ*. These investigators also carried out a comparison of the composition of soil-water extracts with that of the " soil solution " displaced from the soil at different water contents. From this comparison, it appears probable, (1) that the concentration of certain ions, notably chlorine, nitrate, and calcium, in the soil solution *in situ* varies inversely as the moisture content, that is to say, the whole of the chlorine and nitrate exists in the soil in a state of solution, together with an equivalent amount of calcium; (2) that the concentration of phosphate in the soil solution *in situ* is constant for varying moisture contents of the soil, representing a saturation value. This value, however, varies widely from soil to soil; (3) that the concentration of potassium in the soil solution *in situ* is higher in a soil with a low moisture content than in the same soil with a higher moisture content, but not proportionally so. This fact appears to indicate an equilibrium between the potash in the liquid and solid phases, conforming to the general type of Freundlich's absorption equations.

Tulaikov and Kuzmin [41] have described a method of expressing solution from the soil by the use of mechanical pressure combined with suction. Using the older pressure method of Ramann and Van Zyl, Groh [42] has studied the concentration of calcium in the expressed solution, and the influence of season and crops on the results obtained.

The Humic Matter of the Soil.

Eller and his co-workers have carried out an interesting investigation of the properties of the artificial " humic acids " produced by the oxidation of phenols [43] in comparison with those produced by the action of dilute acids on carbohydrates, and with natural humic acids.[44] He advances strong evidence in support of his view that the latter substances are closely related to those produced from phenols, and distinct from those produced from carbohydrates. The arguments advanced earlier by Eller against the presence of

[41] N. M. Tulaikov and M. S. Kuzmin, *Soil Sci.*, 1923, **15**, 235; *A.*, i, 992.

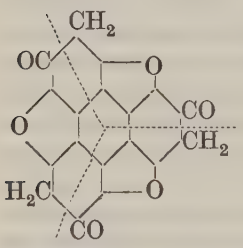
[42] A. W. Groh, *Int. Mitt. Bodenkunde*, 1923, **13**, 107.

[43] Compare *Ann. Rep.*, 1922, **19**, 204.

[44] W. Eller, *Annalen*, 1923, **431**, 133; *A.*, i, 542; W. Eller, H. Meyer, and H. Saenger, *ibid.*, p. 162; *A.*, i, 543; W. Eller, E. Herdieckerhoff, and H. Saenger, *ibid.*, p. 177; *A.*, i, 544. See also P. Stamberger, *Naturprodukte*, 1923, 108; *A.*, i, 1006.

furan nuclei in humic acid are, however, not accepted as valid by Marcusson.[45] Fuchs[46] is of the opinion that natural humic acid contains both furan and phenol nuclei; he also concludes, from the fact that it can be methylated in alkaline solutions without being precipitated, that it contains both phenolic hydroxyl and carboxyl groups. Fischer and Schrader's hypothesis, which regards lignin as the parent substance of humic acid,[47] is somewhat supported by the work of Pictet and Gaulis[48] on the vacuum distillation of lignin.

All these conflicting views as to the nature of humic acid are more or less reconciled by an interesting suggestion by Schrauth,[49] who regards the fundamental unit of lignin as consisting of the annexed nucleus, which besides containing three phenolic hydroxyl groups (in the keto-form) also contains, as shown by the dotted lines, three ω-hydroxymethyl furfural nuclei.[50] This is no more than a working hypothesis at present, but its further development will be awaited with interest.[51]



Biochemical Changes in the Soil.

The Nitrogen Cycle.—An interesting study of various phases of the nitrogen cycle—nitrogen fixation, nitrification, losses of nitrogen—and of biological activity as measured by the evolution of carbon dioxide, in an acid soil in Assam, has been published by Meggitt.[52] The effect of various climatic and soil factors on these processes, and on the nitrogen economy of the soil, under tropical conditions is well brought out.

The fixation of nitrogen by *Azotobacter* has been investigated by Hunter,[53] Gainey,[54] Johnson and Lipman,[55] Voicu,[56] and Truffaut

[45] J. Marcusson, *Z. angew. Chem.*, 1923, **36**, 42; compare *A.*, 1921, ii, 590; 1922, i, 437; 1923, i, 353.

[46] W. Fuchs, *Naturprodukte*, 1923, 98; *A.*, i, 1006.

[47] H. Fischer and H. Schrader, *Brennstoff-Chem.*, 1921, **2**, 3.

[48] A. Pictet and M. Gaulis, *Helv. Chim. Acta*, 1923, **6**, 627; *A.*, i, 758.

[49] W. Schrauth, *Brennstoff-Chem.*, 1923, **4**, 161; *A.*, ii, 502.

[50] C. F. Beckley, *J. Agric. Sci.*, 1921, **11**, 66; *A.*, i, 227.

[51] For a fuller discussion of the nature of the humification process and of its relation to coal formation, see H. J. Page, *Fuel*, 1923, August, p. 232.

[52] A. A. Meggitt, *Mem. Dept. Agr. India, Chem. Ser.*, 1923, i, 31.

[53] O. W. Hunter, *J. Agric. Res.*, 1923, **23**, 665; **24**, 263; *A.*, i, 985; *ibid.*, 1923, **23**, 825.

[54] P. L. Gainey, *ibid.*, **24**, 185; *A.*, i, 881; P. L. Gainey and H. W. Batchelor, *ibid.*, p. 759; P. L. Gainey, *ibid.*, p. 289, 907; *A.*, i, 1166.

[55] H. W. Johnson and C. B. Lipman, *Univ. California Pub. Agr. Sci.*, 1922, **4**, 397; *A.*, i, 633.

[56] J. Voicu, *Compt. rend.*, 1923, **176**, 1421; *A.*, i, 735.

and Bezssonoff.[57] Hunter found that growth was increased by aëration, and that the protein content of the cells was thereby almost trebled. In continuation of earlier work, Gainey has shown that soils with a hydrogen-ion concentration greater than that corresponding to p_H 6·0 cannot support the growth of *Azotobacter*, and that the most favourable reaction for nitrogen fixation is p_H 6·5, although Johnson and Lipman [55] placed this value between p_H 7·0 and 8·0. These investigators found, however, that between p_H 6·2 and 8·8 there was but little variation in the amounts of nitrogen fixed, but that outside this range slight changes in p_H caused an abrupt decrease in fixation. Voicu has shown that humus has a marked stimulating effect on the fixation of nitrogen by *Azotobacter*, whilst Truffaut and Bezssonoff find that the development of this organism and also that of *Bacillus Truffauti*, both aërobic organisms, are most favoured by concentrations of sugar of the order of 0·1 per cent. rather than by higher concentrations, the converse being true of the corresponding anaërobic bacilli.

The work of Wann,[58] as a result of which he claimed to have shown that green algæ were able to assimilate atmospheric nitrogen in the presence of nitrates, has been critically repeated by Bristol and Page [59] at Rothamsted. These investigators entirely failed to obtain evidence of any fixation of nitrogen by green algæ, although the conditions of the experiment were as nearly as possible identical with those used by Wann. Moreover, they showed that the methods of analysis used by Wann were faulty, and that it was possible to explain the whole of the apparent fixation in Wann's results as due to analytical errors. Whilst still admitting the possibility that green algæ might fix atmospheric nitrogen, they point out that there is still no conclusive evidence in favour of the occurrence of this action. The function of the green algæ in the soil must therefore be sought in some other direction.

Nasir [60] has obtained evidence that the fixation of nitrogen by *Azotobacter* in liquid or sand cultures is stimulated by the presence of soil protozoa.

Unlike nitrogen fixation and nitrification, the process of ammonification is not brought about by a specific organism or group of organisms, but by a large number of different species of bacteria and also by fungi. Abbott [61] has isolated twenty-eight species of fungi, representing twelve genera, from five Iowa soils. With two exceptions all the species showed vigorous ammonifying power.

[57] G. Truffaut and N. Bezssonoff, *ibid.*, 1923, **177**, 649; *A.*, i, 1268.
[58] F. B. Wann, *Amer. J. Bot.*, 1922, **8**, 1.
[59] (Miss) B. M. Bristol and H. J. Page, *Ann. Appl. Biol.*, 1923, **10**, 378.
[60] S. M. Nasir, *Ann. Appl. Biol.*, 1923, **10**, 122.
[61] E. V. Abbott, *Soil Sci.*, 1923, **16**, 207; *A.*, i, 1167.

Soil moulds are very tolerant of acid conditions, as illustrated by the work of Johnson,[62] so that they probably play an important part in ammonification in sour soils. Waksman [63] has studied the ammonifying power of various soils in solution and in the soil itself; he concludes that owing to the variety of the organisms concerned, and to the fact that the process is influenced by so many other factors, ammonification in solution or in soil cannot be used as an index of soil fertility. From a study of the nitrifying power of various soils, however, the same investigator [64] concludes that this power is in general an indication of the productivity of the soil.

The mechanism of the bacterial nitrification process, whereby ammonia is oxidised first to nitrous and then to nitric acid, has up to now resisted all attempts at its elucidation. The existence of an extracellular ammonia-oxidising enzyme or " nitroxidase," whereby the organism is supposed to convert ammonia into nitrous acid, has never been demonstrated. Bonazzi,[65] however, has now carried out a suggestive investigation using a pure culture of an active form of *Nitrosococcus*, in which he has shown (1) that the ratio O/N, where O is the quantity of oxygen absorbed by the culture, and N is the quantity of nitrogen nitrified, both expressed as gram-atoms, is equal to 3, which is in accordance with the symbolisation of the process as $NH_3 + 3O \longrightarrow HNO_2 + H_2O$; (2) that iron, which is known to be essential to the action, is reduced from the ferric to the ferrous state, in active cultures; (3) that in faintly alkaline solution hydrogen peroxide is able to oxidise ammonium salts to nitrites; (4) that although no evidence can be obtained for the existence of either a peroxide or a peroxydase in the culture liquid itself, a culture containing active *Nitrosococcus* or even the dead bacterial cells, killed and washed by treatment with acetone and ether, can under alkaline conditions catalyse the decomposition of hydrogen peroxide, but this property is lost after heating. On the basis of these results, Bonazzi formulates the following hypothesis: iron exists in the bacterial cell in the ferrous state, in which form it acts as an oxygen carrier owing to its ready conversion into ferrous oxide peroxide; accepting Bach and Chodat's conception of oxydase action, it is concluded that the iron by its mechanism of auto-oxidation fulfils the functions of the peroxide, whilst the breakdown of this peroxide with liberation of " active " oxygen is accomplished by a mechanism inherent in the cell itself—an intracellular per-oxydase. The evidence is at present rather circumstantial, but the hypothesis is an attractive one, and will no doubt serve as a valuable stimulus to further work.

[62] H. W. Johnson, *Iowa Agr. Sta. Research Bull.*, 76, 1923.
[63] S. A. Waksman, *Soil Sci.*, 1923, **15**, 49.
[64] *Idem, ibid.*, **16**, 55.
[65] A. Bonazzi, *J. Bact.*, 1923, **8**, 343.

The autotrophic character of the nitrifying organisms in liquid cultures, whereby they derive their carbon from carbon dioxide, with the aid of the energy liberated in the oxidation of ammonia, is an important factor in the process. The bearing of this factor on the gaseous exchange of the organism does not appear to have been considered by Bonazzi, although it would appear probable that a part of the oxygen utilised for the conversion of ammonia into nitrate would be derived from that liberated from the carbon dioxide in its assimilation by the organism. This oxygen would be so to say "internal," and would not figure on the gaseous exchange. In view, however, of the fact that the ratio of ammonia nitrogen oxidised to carbon assimilated was found by Winogradsky to be of the order of 35,[66] this factor would not seriously affect the validity of the conclusions Bonazzi drew from the value found by him for the ratio O/N in the gaseous exchange; it might even account for the slight defect of the experimental value ($2{\cdot}89 \pm 0{\cdot}08$) from the theoretical value of 3·0.

The nitrate content of the soil at any time is the resultant of two opposing sets of factors, one set being concerned with the production of nitrate, and the other with its removal. It is well known that the soil shows a seasonal fluctuation in its nitrate content, maxima occurring in the spring and autumn, and minima in winter and summer. Schönbrunn [67] concludes from the results of an investigation into this question that these seasonal fluctuations are conditioned solely by seasonal changes in the environmental factors such as soil temperature, rainfall, and so on, and that there is no *inherent* periodicity in these processes. Schönbrunn's work and conclusions have been, however, strongly assailed by Löhnis [68] who, whilst admitting the influence of environmental factors, is of the opinion that there is some evidence also for an inherent seasonal periodicity in the activity of the organisms themselves.

Other factors that influence the credit side of the nitrogen balance sheet are the reaction of the soil and the content of salts. Meek and Lipman [69] have shown that the nitrifying organisms are particularly resistant to hydroxyl-ions, surviving in a medium of p_H 13, and remaining active in a medium of p_H 11. Among various sodium salts tested, sodium sulphate was not nearly so toxic as sodium chloride or sodium carbonate.

On the debit side of the nitrogen balance sheet there is a variety of factors operative. In addition to actual losses of nitrogen from

[66] S. Winogradsky, *Ann. Inst. Pasteur*, 1890, **4**, 213, 257.

[67] B. Schönbrunn, *Zentr. Bakt. Par.*, 1922, **56**, ii, 545; from *Chem. Zentr.*, 1923, I, 1606; *A.*, i, 1167.

[68] F. Löhnis, *Zentr. Bakt. Par.*, 1923, **58**, ii, 207; from *Chem. Zentr.*, 1923, I, 1606; *A.*, i, 1167.

[69] C. S. Meek and C. B. Lipman, *J. Gen. Physiol.*, 1922, **5**, 195; *A.*, i, 74.

the soil, such as those due to absorption by plants and to drainage, and to denitrifying organisms [70] and other processes which give rise to gaseous nitrogen, various biological processes result in the conversion of soluble nitrogen (nitrates) in the soil into insoluble forms not immediately available for plant growth. This conversion occurs pre-eminently when organic matter of low nitrogen content is added to the soil, as illustrated by the effect of straw, which is confirmed by the results of Sievers.[71] This type of action is regarded by Lyon, Bizzell, and Wilson [72] as the cause of the well-known effect of growing plants in depressing nitrate accumulation in the soil to an extent greater than that accounted for by their own absorption of nitrate; this effect has sometimes been regarded in the past as an indication of a depressing effect of the growing plant on nitrate formation, but the above investigators advance evidence in favour of the view that the organic matter derived from the roots of growing plants is often of low nitrogen content, and thus favourable to the action of nitrate-consuming soil organisms, and that the variation in the depressive effect of different plants on nitrate accumulation may be correlated with the variations in the nitrogen content of the organic matter derived from their roots. In other words, the effect of the growing plant is not one of inhibition of nitrate *production*, but one of the stimulation of nitrate *consumption*, by soil organisms. The well-known effect of the growth of grass around fruit trees, in depressing the vitality and yield of the trees, on which Pickering did so much work [73] has been studied by Lyon, Heinicke, and Wilson,[74] whose results appear to show that this effect also is due, at least in part, to the biological conversion of nitrate into insoluble nitrogen compounds in the soil in the manner just discussed, resulting in nitrogen starvation of the tree.

It must be emphasised that processes of this type do not deplete the soil as a whole of nitrogen, but only of available nitrogen. They figure in the nitrogen balance sheet as a transfer to capital account rather than as an actual expenditure.

The Sulphur Cycle.—The oxidation of sulphur to sulphuric acid in the soil by specific autotrophic bacteria, which has been extensively studied by J. G. Lipman and his co-workers at New Jersey,[75] still

[70] See, for example, C. Lumia, *Annali Chem. Appl.*, 1923, **7**, 155.

[71] F. J. Sievers, *Washington Agric. Expt. Sta. Bull.*, 1922, **167**, 45; *A.*, i, 1048.

[72] T. L. Lyon, J. A. Bizzell, and B. D. Wilson, *J. Amer. Soc. Agron.*, 1923, **15**, 457. See also J. A. Bizzell, *ibid.*, 1922, **14**, 320; *A.*, i, 522.

[73] S. U. Pickering and the Duke of Bedford, Reports of Woburn Expt. Fruit Farm, 3rd Report, 1903; 13th Report, 1911; 14th Report, 1914.

[74] T. H. Lyon, A. J. Heinicke, and B. D. Wilson, *Cornell Univ. Agri. Expt. Sta.* Memoir 63, 1923.

[75] See *Ann. Rep.*, 1922, **19**, 209.

provokes a considerable amount of research.[76] Waksman and Starkey[77] have studied the growth and respiration of *Sulphomonas thio-oxidans*. They find that in the oxidation of sulphur and of sodium thiosulphate the ratio of sulphur oxidised and carbon dioxide reduced is 31·8 and 64·2, respectively. Lipman and Waksman[78] have also described an analogous group of autotrophic bacteria which oxidise selenium to selenic acid.

Phosphates have been shown to be liberated from nucleo-proteins and their breakdown products by various soil bacteria (nucleobacter).[79]

Partial Sterilisation.—Broadly speaking, the effect of partial sterilisation on the soil is the resultant of four main groups of factors, thus :

(1) The removal of factors inimical to the growth of bacteria.

(2) The direct liberation of plant food from the soil by the action of the partial sterilising agent.

(3) The direct stimulation of the growth of certain groups of bacteria by the feeding effect on them of the sterilising agent itself (for example, phenol).

(4) The removal of factors inimical to plant growth (for example, plant disease organisms).

Waksman has carried out a series of investigations[80] with a view to the elucidation of the relative importance of these factors. He concludes from his results that the part played by the soil fungi is more important than is generally realised; he ascribes the limitation of bacterial numbers in untreated soil largely to the competition for nutrient material between the fungi and the bacteria. The soil fungi are very greatly reduced in numbers on partial sterilisation, and the bacteria are thus, in his view, enabled to multiply to much greater numbers when free from the competitive action of the fungi. He considers that although protozoa may limit bacterial development in abnormal soils such as greenhouse soils, such an inhibition is improbable in ordinary soils. Against this, however, must be reckoned the fact that Cutler, Cruup, and Sandon[81] were able to demonstrate the inverse relationship between the number of

[76] See, for example, H. O. Brown, *J. Amer. Soc. Agron.*, 1923, **15**, 350. See also *Ann. Rep. Appl. Chem.* (*Soc. Chem. Ind.*), 1923, **8**, where the practical applications are discussed.

[77] S. A. Waksman and R. L. Starkey, *J. Gen. Physiol.*, 1923, **5**, 285; *A.*, i, 273.

[78] J. G. Lipman and S. A. Waksman, *Science*, 1923, **57**, 60; *A.*, i, 735.

[79] A. Koch and A. Oelsner, *Biochem. Z.*, 1922, **134**, 76; *A.*, i, 422.

[80] S. A. Waksman and R. L. Starkey, *Soil Sci.*, 1923, **16**, 137, 247, 343; *A.*, i, 1167.

[81] See *Ann. Rep.*, 1922, **19**, 218.

protozoa and bacteria in a field soil; further, Cutler [82] has now shown that the same phenomenon can be demonstrated by the inoculation of sterilised field soil with bacteria alone and with a mixture of bacteria and protozoa. Where bacteria alone were used, the numbers remained high, but when protozoa were also added, the numbers of bacteria fell very considerably. From these facts it would appear that protozoa cannot be left out of account as a factor limiting bacterial numbers in field soils.

Baldwin [83] has studied the effect of crude petroleum on the soil micro-flora, and on ammonification and nitrification.

Other Soil Constituents.

Griffiths-Jones [84] has found that the titanium content of Nile silt is from 1·3—2·5 per cent. Wester [85] has studied the manganese content of some Dutch soils, which varied from a trace up to 120 mg. per 100 grams of dried soil. Generally the more fertile soils were richer in manganese than the less fertile.

Kunz-Krause [86] has described the occurrence of a greyish-blue coloration on arable soil near Dresden. This he ascribes to the presence of blue basic ferric ferrous phosphate (vivianite) formed from colourless ferrous phosphate by oxidation in air.

Iron and manganese, together with humic substances, would appear to be the agents chiefly responsible for the power of soils to decompose hydrogen peroxide, the effect of bacteria and of enzymes being less important.[87]

The Soil as a Medium for Plant Growth.

So far in this Report we have dealt with soil processes and properties, *per se*, mainly without reference to the plant. The influence of soil and associated factors on the growing plant will next be considered.

The concentration of the soil solution has an important effect on plant growth. This has been studied by Tulaikov.[89] There is an optimum value for plant growth, and an increase above this optimum caused delayed germination of seeds and weakened growth of seedlings; it also caused in his experiments on cereals an increased nitrogen content of the crop and a greater hardness of the grain. The characteristic hardness of wheat from Russia and the arid

[82] D. W. Cutler, *Ann. Appl. Biol.*, 1923, 10.
[83] I. L. Baldwin, *Soil Sci.*, 1922, **14**, 465.
[84] E. Griffiths-Jones, *Analyst*, 1923, **48**, 320.
[85] D. H. Wester, *Pharm. Weekblad*, 1923, **60**, 446; *A.*, i, 640. See also *Internat. Mitt. Bodenkunde*, 1923, **13**, 1.
[86] H. Kunz-Krause, *Ber. Deut. pharm. Ges.*, 1923, **33**, 20; *A.*, ii, 325.
[87] S. Osugi, *Ber. Ohara Inst. Landw. Forsch.*, 1922, **2**, 197; *A.*, i, 524.
[89] N. M. Tulaikov, *Soil Sci.*, 1923, **15**, 229; *A.*, i, 992.

regions of the United States is regarded by this investigator as due to the high osmotic pressure of the soil solution in those areas. Shive [90] has studied the inter-relation between the osmotic pressure of the soil solution and the ratio of the various ions (" physiological balance ") with regard to their effect on the yield. The most favourable physiological balance is about the same for appreciable variations in total concentration. Variations of the latter type are just as important as changes in the physiological balance, from the point of view of crop yield; the effect of unfavourable moisture conditions cannot be counteracted by altering the physiological balance by special fertiliser treatment.[91]

A special case of the influence of the ratio of the different bases in the soil on plant growth is the so-called " potash lime law " of Ehrenberg,[92] according to which the amount of potash taken up by the plant is reduced by treatment with lime, so that in soils which are poor in potash liming may depress the crop. Fischer [93] has studied this phenomenon in pot experiments with various crops; in general, his results confirm Ehrenberg's conclusions.

It is commonly supposed that sodium can replace potassium to a certain extent in plants, seeing that in soils which are potash starved, manuring with sodium salts usually gives bigger yields than when it is omitted. This may be partly due to liberation of potash from the soil by basic exchange (see p. 204), but this does not appear to explain the whole effect. Sodium chloride seems to have a beneficial effect on some leguminous crops; in the case of lucerne this has been demonstrated by Lomanitz [94] in water culture, where basic exchange phenomena are excluded, whilst a somewhat analogous result is that obtained with red clover by Emerson and Barton,[95] who found that the potassium of kainit, which contains a large excess of sodium chloride, was more readily absorbed than that of high grade chloride or sulphate of potash. Marschhaupt [96] found, however, that in the case of turnips the potash content fell with increasing quantity of sodium in the soil, and *vice versa*. Sodium chloride is usually supposed to have a favourable effect on the development of sugar beet—a plant of maritime origin—but Meyer [97] could find no

[90] J. W. Shive, *ibid.*, 1922, **14**, 391; *A.*, i, 283.

[91] For other work on similar lines, see A. L. Bakke and L. W. Erdman, *Amer. J. Bot.*, 1923, **10**, 18; *New Mexico Agr. Expt. Sta. Ann. Rep.*, 1921, 24; *A.*, i, 1048.

[92] P. Ehrenberg, *Landw. Jahrb.*, 1919, **54**, 4.

[93] W. Fischer, *ibid.*, 1923, **58**, 1. [94] S. Lomanitz, *Soil Sci.*, 1923, **16**, 183.

[95] P. Emerson and J. Barton, *J. Amer. Soc. Agron.*, 1922, **14**, 182; *A.*, i, 522.

[96] J. G. Marschhaupt, *Versl. Landbouwk. Onders. Rijklandbouwproefstat.*, Sept., 1923.

[97] D. Meyer, *Z. Pflanz. Düng.*, 1923, **2**, *B*, 446.

evidence for such an effect in his experiments. In all work of this sort the type of soil and the species of plant have such an important influence on the result that the conflicting results often obtained by different investigators are not at all surprising.

The relation of the hydrogen-ion concentration of the soil to plant growth is a complex one. Although there can be no question of the direct toxic effect of an excessive concentration of hydrogen- or hydroxyl-ions,[98] opinions differ with regard to the nature of the toxicity in cases where that concentration is not excessive, although still appreciable. The effect may still be a direct one, as supposed by Olsen,[99] the concentration of hydrogen- or hydroxyl-ions influencing the absorption of nutrient salts by the plant root, or it may be due to secondary effects, owing to the correlation of the soil reaction with the concentration of nutrient or toxic substances in the soil solution. This latter alternative is illustrated by the view originally advanced by Hartwell and Pember,[1] who suggested that the toxicity of acid soils was due to the soluble aluminium they contained. This view is gaining ground, especially in the United States,[2] iron and manganese being included in the same category as aluminium. Although the concentration of soluble iron in a sour soil may thus be so high as to be toxic, in an alkaline soil the position may be reversed, and the iron may be rendered so insoluble that chlorosis occurs in the plant. This is shown by the work of Willis and Carrero,[3] Barnette and Shive,[4] and Jones and Shive,[5] in which is also illustrated the important difference between a "physiologically alkaline" fertiliser like nitrate of soda, which leaves an alkaline residue in the soil and thus tends to cause chlorosis, and a "physiologically acid" fertiliser like sulphate of ammonia, which does not cause chlorosis, but which, if used continually in absence of lime, sets up excessively acid conditions. Reference may also be made to the use of physiologically acid fertilisers in conjunction with insoluble phosphates as a means of improving the availability of the latter.[6]

[98] See, for example, O. C. Bryan, *Soil Sci.*, 1923, **15**, 375.

[99] C. Olsen, *Compt. rend. Trav. Lab. Carlsberg*, 1923, **15**, 1; *A.*, i, 522. See also A. P. Kelley, *Soil Sci.*, 1923, **16**, 41.

[1] Hartwell and Pember, *Soil Sci.*, 1914, **6**, 259.

[2] J. W. Kelly, *J. Agric. Res.*, 1923, **23**, 223; R. H. Carr and P. H. Brewer, *Ind. Eng. Chem.*, 1923, **15**, 634; *A.*, i, 1275; A. W. Blai and A. L. Prince, *Soil Sci.*, 1923, **15**, 109; P. L. Gile, *J. Amer. Soc. Agron.*, 1923, **15**, 305.

[3] L. G. Willis and J. O. Carrero, *J. Agric. Res.*, 1923, **24**, 621.

[4] R. M. Barnette and J. W. Shive, *Soil Sci.*, 1923,. **15**, 413.

[5] L. H. Jones and J. W. Shive, *Ann. Bot.*, 1923, **37**, 355; *A.*, i, 1043.

[6] See *Ann. Rep. Appl. Chem.* (*Soc. Chem. Ind.*), 1923, **8**. For other work on the question of soil reaction, see A. Gehring and F. Sander, *Z. Pflanz. Düng.*, 1923, II, *B*, 299; F. Munter, *ibid.*, p. 289.

Atkins [7] has brought forward evidence that the influence of soil acidity in causing the flowers of the hydrangea to become blue may also be due to the increased availability of the iron in such a soil, the iron taken up by the plant giving a blue complex with the anthocyanin flower pigment.

A sufficient supply of oxygen to the plant root is known to be necessary for healthy growth. The rate at which oxygen can reach the root through the soil depends on the physical condition of the soil and its moisture content. Hutchins and Livingstone [8] have described an apparatus for measuring the oxygen-supplying power of the soil, based on diffusion into a porous cylinder buried in the soil, the oxgyen being continually swept out of the cylinder by an inert gas, and passed through alkaline pyrogallol.

Stimulants and Toxic Agents.—In the case of certain elements one cannot at present discriminate between the alternative possibilities of their acting as true plant nutrients, or as stimulants, the latter term being used merely in the sense of indicating that the cause of the stimulating effect of the element in question is unknown.

Additional support for the view that silica is of value to the plant [9] is afforded by the results of Schollenberger.[10] Boron has long been known to exert a toxic effect on plants above a certain concentration; [11] as a result of recent work at Rothamsted, however, Miss Warrington [12] has demonstrated that small amounts of boron are not merely stimulating, but essential for the development of the broad bean and certain other leguminous plants, when grown in water culture. The results are very striking: very marked response is observed at concentrations of boric acid ranging from 1 : 25,000 to as low as 1 : 12,500,000. The same results are not usually obtained in soil cultures owing to the common occurrence of boron in most ordinary soils. For other crops, such as barley, there is no evidence that boron is necessary.

There is already evidence that manganese is of value to the plant, in minimal concentrations,[13] although in higher concentrations it is harmful. This is supported by the results of McHargue,[14] who finds that leguminous plants are specially responsive, and of Picado and Vicente.[15] According to Rippel,[16] the toxic effect of higher

[7] W. R. G. Atkins, *Sci. Proc. Roy. Dubl. Soc.*, 1923, **17**, 201; *A.*, i, 1162.

[8] L. M. Hutchins and B. E. Livingstone, *J. Agric. Res.*, 1923, **25**, 133; *A.*, ii, 66.

[9] See *Ann. Rep.*, 1922, **19**, 215.

[10] C. J. Schollenberger, *Soil Sci.*, 1922, **14**, 347.

[11] See, *e.g.*, J. J. Skinner and F. E. Allison, *J. Agric. Res.*, 1923, **23**, 433.

[12] K. Warington, *Ann. Bot.*, 1923, **37**, 629; *A.*, i, 1274.

[13] See W. E. Brenchley, *Ann. Bot.*, 1910, **24**, 521.

[14] J. S. McHargue, *J. Agric. Res.*, 1923, **24**, 781; *A.*, i, 1160.

[15] E. Picado and E. Vicente, *Ann. Inst. Pasteur*, 1923, **37**, 891; *A.*, i, 1276.

[16] A. Rippel, *Biochem. Z.*, 1923, **140**, 315; *A.*, i, 1160.

concentrations of manganese is due to iron chlorosis, the manganese apparently influencing, not the intake of iron, but its availability after absorption by the plant. The assimilation by the broad bean of lead, which is toxic in concentrations of $N/10$ or above, has been studied by Hevesy [17] by a method depending on the admixture with the lead salt of a radioactive isotope (thorium *B*), the amount of lead taken up being estimated by measuring the radioactive intensity of the ash.

Němec and Káš [18] report the result of pot experiments from which it appears that the growth of mustard, peas, and lucerne was stimulated by the addition to the soil of titanium in the form of sodium titanate or titanocitrate.

Hexamethylenetetramine is a nutrient for the broad bean in small doses, but in higher concentrations than 0·3 gram per litre it is toxic.[19] In the soil it is readily broken down into ammonia by soil organisms.[20]

The Chemistry of the Living Plant.

Carbon Assimilation.—The formation of formaldehyde from carbon dioxide solutions by the action of sunlight in presence of colloidal oxides of uranium or ferric iron, as observed by Moore and Webster [21] and confirmed by Baly, Heilbron, and Barker,[22] could not be detected by Baur and Rebmann.[23] Similarly, Spoehr [24] could not repeat Baly, Heilbron, and Barker's observation of the action of ultra-violet light in causing the formation of formaldehyde from carbon dioxide in aqueous solution. The latter investigators, however, have repeated their earlier work with the same results as before, and they suggest that Spoehr's failure may have been due to deterioration of the quartz mercury lamp employed.[25]

Maquenne [26] has put forward a theory of chlorophyllic photosynthesis which is supposed to get over the difficulty that the presence of formaldehyde in plants has never been indubitably proved. His theory depends on the assumption of a combination of carbon dioxide

[17] G. Hevesy, *Biochem. J.*, 1923, **17**, 439; *A.*, i, 1160.

[18] A. Němec and V. Káš, *Biochem. Z.*, 1923, **140**, 583; *A.*, i, 1161.

[19] E. Nicolas and G. Nicolas, *Compt. rend.*, 1922, **175**, 836; **176**, 404; *A.*, i, 77, 427.

[20] E. Blanch, W. Geilmann, and F. Giesecke, *J. Landw.*, 1922, **70**, 221; *A.*, i, 171.

[21] B. Moore and T. A. Webster, *Proc. Roy. Soc.*, 1913, [*B*], **87**, 163; *A.*, 1913, i, 1303.

[22] *T.*, 1921, **119**, 1025.

[23] E. Baur and A. Rebmann, *Helv. Chim. Acta*, 1922, **5**, 828; *A.*, i, 91.

[24] H. A. Spoehr, *J. Amer. Chem. Soc.*, 1923, **45**, 1184; *A.*, ii, 452.

[25] E. C. C. Baly, I. M. Heilbron, and W. F. Barker, *Nature*, 1923, **112**, 323.

[26] L. Maquenne, *Compt. rend.*, 1923, **177**, 853; *A.*, i, 1272.

with the magnesium atoms in the chlorophyll molecule; the resulting complex is assumed to undergo isomeric change, followed by loss of oxygen, polymerisation, and the splitting off of carbohydrate. One essential difference between this view and that of Baly and his co-workers is that, according to the former, the polymerisation of the formaldehyde units is supposed to occur inside the chlorophyll complex, whereas Baly's view is that, although the carbon dioxide combines with the chlorophyll, and is photocatalytically reduced to formaldehyde in virtue of that combination, the formaldehyde itself is liberated in an active form (as H–C–OH) which immediately polymerises.

Thunberg [27] has advanced another explanation of the mode of formation of formaldehyde; he supposes that the first action is the decomposition of water by sunlight to give hydrogen peroxide and hydrogen. These then react with carbon dioxide to give methylene glycol, thus : $CO_2 + H_2 + H_2O_2 = H_4CO_2 + O_2$, and the methylene glycol loses water to give formaldehyde.. There is not at present sufficient experimental evidence available to enable the relative merits of these rival hypotheses to be tested.

The energetics of the reactions postulated by Thunberg have been discussed by Weigert,[28] whilst Warburg and Negelein [29] have investigated the influence of wave-length on the energy change of carbon dioxide assimilation in presence of chlorophyll.

Bose [30] has shown that the photosynthetic activity of the aquatic plant *Hydrilla verticillata* was very greatly increased by nitric acid in concentrations between 1 in 10^{10} and 1 in 2×10^9. Similar increases were obtained by the application of dilute solutions of thyroid gland extract and of formaldehyde, the latter substance producing a marked effect in a concentration of 1 in 10^9. Sabalitschka [31] has described experiments from which it appears that the nasturtium and the water weed *Elodea canadensis* can fix formaldehyde and polymerise it to carbohydrate even in the absence of light.

Spoehr and McGee [32] have published an account of a lengthy investigation on the inter-relation between photosynthesis and respiration, from which they conclude that photosynthesis may be a dual or coupled reaction. The original must be referred to for details.

[27] T. Thunberg, *Z. physikal. Chem.*, 1923, **106**, 306; *A.*, i, 1271.

[28] F. Weigert, *ibid.*, p. 313; *A.*, i, 1271.

[29] O. Warburg and E. Negelein, *ibid.*, p. 191; *A.*, ii, 718.

[30] J. C. Bose, *Nature*, 1923, **112**, 95; *A.*, i, 1043. See also E. and G. Nicolas, *Compt. rend.*, 1922, **175**, 1437.

[31] T. Sabalitschka, *Z. angew. Chem.*, 1922, **35**, 684; *A.*, i, 76.

[32] H. A. Spoehr and J. M. McGee, *Carnegie Inst. Pub.*, 1923, **325**, 1; *A.*, i, 988.

Mitscherlich has published a suggestive paper on the principles underlying the use of atmospheres artificially enriched with carbon dioxide as a means of obtaining increased yields of plants.[33]

Synthesis and Translocation of Complex Carbon and Nitrogen Compounds.—In continuation of their work on the photocatalytic formation of nitrogen compounds,[34] Baly and his co-workers [35] have now studied the action of activated formaldehyde on ammonia, both by exposing to ultra-violet light a solution of carbon dioxide in ammonia and by the use of daylight and a solution of carbon dioxide in ammoniacal cupric carbonate, the coloured copper–ammonium complex acting as the photocatalytic energy transformer. They obtained in this way solutions from which they isolated methylamine, pyridine, and piperidine, and an alkaloidal base which they claim to have identified with coniine by chemical and physiological tests. These results have, however, been challenged by Snow and Stone,[36] who, whilst not denying the possibility of the photocatalytic formation of the nitrogen compounds isolated by Baly, adduce evidence that they may have been the result of secondary reactions during the operations used for working up the solutions, and that the identification of the coniine-like alkaloid was not conclusive. Baudisch, whose work on the interaction of nitrites with activated formaldehyde to give formhydroxamic acid, methylamine, and amino-acids, etc., was confirmed by Baly and his co-workers,[37] has studied the mechanism of the reduction of nitrates to nitrites,[38] in which he claims to show that iron plays an essential part.

Prianischnikov [39] has further developed his earlier theories on the nitrogen metabolism of plants. Asparagine is held to perform the same function in plant metabolism as urea in animal metabolism. In seedling plants receiving ammonium salts, the amount of asparagine formed depends on the amount of carbohydrate available. Amino-acids and proteins are supposed to be formed from asparagine in presence of carbohydrates, and the process is held to be reversible, so that in absence of carbohydrates degradation of protein to asparagine or glutamine and finally to ammonia occurs. Similar views are advanced by Smirnov.[40] Roberts [41] has shown, in the

[33] E. A. Mitscherlich, *Z. Pflanz. Düng.*, 1923, **2**, *A*, 211. For a discussion of the practical aspects of this question, see *Ann. Rep. Appl. Chem.* (*Soc. Chem. Ind.*), 1923, **8**.

[34] See *Ann. Rep.*, 1922, **19**, 220.

[35] E. C. C. Baly, I. M. Heilbron, and H. J. Stern, *T.*, 1923, **123**, 185.

[36] O. W. Snow and J. F. S. Stone, *T.*, 1923, **123**, 1509.

[37] See *Ann. Rep.*, 1922, **19**, 220.

[38] O. Baudisch, *Science*, 1923, **57**, 451; *A.*, ii, 816.

[39] D. N. Prianischnikov, *Landw. Versuchs-stat.*, 1922, **99**, 267; *A.*, i, 425; *Ber. Deut. bot. Ges.*, 1922, **40**, 242; *A.*, i, 273.

[40] A. I. Smirnov, *Biochem. Z.*, 1923, **137**, 1; *A.*, i, 636.

[41] R. H. Roberts, *Proc. Amer. Soc. Hort. Sci.*, 1921, 143; from *Physiol. Abstr.*, 1923, **8**, 107; *A.*, i, 884.

case of apple trees, that carbohydrates decrease with an increase in nitrogen content and *vice versa*. Chibnal [42] concludes from a review of the literature that the withdrawal of nitrogen from the leaves of the plant occurs at night. The movement of nitrogen and of carbohydrates in the wheat plant during growth and ripening has been studied by Olsen [43] and by Colin and Belval,[44] respectively.

In 1920, Parker and Truog advanced the hypothesis that there is an intimate relationship between the *rôles* of calcium and nitrogen in plant nutrition.[45] They supposed that the synthesis of protein in plants involves the production of by-product organic acids which are neutralised and precipitated by calcium, so that the amount of calcium taken up is directly related to the amount of protein formed in the plant. They instanced the case of leguminous plants which are high in calcium content as well as in nitrogen. This hypothesis has now been tested by Newton.[46] His results do not support it, since in water cultures the intake of calcium by such plants as barley and peas was not proportional to the nitrogen content. They explain the high calcium content of leguminous plants when grown on soil as due to the much larger amounts of carbon dioxide evolved by the roots of such plants, in comparison with non-legumes, this resulting in an increase in the solubility of calcium in the soil and thus in an increased calcium intake which does not necessarily bear any relation to the nitrogen content. Although these arguments are not entirely conclusive, they render further work necessary before Parker and Truog's hypothesis can be accepted.

Werner [47] has directed attention to the presence of urease in the root nodules of various leguminous plants, whilst Beijerinck [48] has shown that urease is produced more profusely by pure cultures of *Bacterium radicicola* than by nodules.[49] These results may have an important bearing on the process of nitrogen fixation by the nodule organism.

Miss Semmens [50] has demonstrated a curious effect of plane-polarised light on the hydrolysis of starch in the mustard seed and also of starch grains when acted on by diastase *in vitro*. Iljin [51]

[42] A. C. Chibnall, *Ann. Bot.*, 1923, **37**, 511; *A.*, i, 1045.
[43] G. A. Olsen, *J. Agric. Res.*, 1923, **24**, 939; *A.*, i, 1164.
[44] H. Colin and H. Belval, *Compt. rend.*, 1922, **175**, 1441; *A.*, i, 282.
[45] F. W. Parker and E. Truog, *Soil Sci.*, 1920, **10**, 49.
[46] J. D. Newton, *ibid.*, 1923, **15**, 181.
[47] E. A. Werner, *Nature*, 1923, **112**, 202; *A.*, i, 1046.
[48] M. W. Beijerinck, *ibid.*, p. 439; *A.*, i, 1157.
[49] See also H. E. Armstrong, *Nature*, 1923, **112**, 620; *A.*, i, 1275.
[50] E. S. Semmens, *Chemistry and Industry*, 1923, **42**, 954; *A.*, ii, 718.
[51] W. S. Iljin, *Biochem. Z.*, 1922, **132**, 494, 511, 526; *A.*, i, 172.

has studied the effect of various kations and anions on the hydrolysis and synthesis of starch in vegetable cells, and the antagonism between ions in this process.

Germination.—Baker and Hulton [52] and also Loibl [53] have discussed the nature of the chemical changes involved in the mobilisation of carbohydrate and nitrogen reserves in the germination of cereal grains. Tamhane [54] has made a similar study of the germination of safflower seed. Bach and Oparin [55] have investigated the rate at which the content of respiratory and hydrolytic enzymes rises during the germination of wheat and sunflower seeds.

From an investigation of the mobilisation of mineral substances and nitrogen during the sprouting of shoots of *Sambucus nigra*, Rippel [56] concludes that the potassium, phosphate, and nitrogen are strongly mobilised, magnesium and soda to a lesser extent, and calcium, sulphur, and chlorine scarcely at all.

Respiration.—Apparatus for the study of gaseous exchange during the respiration of plants and seeds has been described by Fernandes [57] and by Harrington and Crocker.[58] Using the apparatus of the latter investigators, Harrington has studied the respiration of apple seeds under different conditions.[59] At the ordinary temperature, the respiratory quotient corresponds to complete oxidation of fats or only slight increase in sugars; with advancing germination the respiratory quotient becomes low, indicating the rapid transformation of fats and accumulation of sugars.

In a series of papers [60] the effects of lactic acid, chloroform, hydrogen peroxide, ferric sulphate, and various other salts on respiration have been investigated. It is concluded that lactic acid is not an intermediate substance in the metabolism of wheat seedlings. Analogies are also drawn between the effect of chloroform on plant respiration and on the oxidation of organic acids by hydrogen peroxide and ferrous sulphate.

[52] J. L. Baker and H. F. E. Hulton, *J. Inst. Brewing*, 1923, **29**, 824.

[53] H. Loibl, *Z. ges. Brauwesen*, 1923, **46**, 30, 37, 45, 53, 61, 69; from *Chem. Zentr.*, 1923, III, 396; *A.*, i, 1270.

[54] V. A. Tamhane, *Mem. Dept. Agric. India*, 1923, **6**, 223; *A.*, i, 883.

[55] A. Bach and A. Oparin, *Biochem. Z.*, 1922, **134**, 183; *A.*, i, 425.

[56] A. Rippel, *ibid.*, 1923, **135**, 518; *A.*, i, 521.

[57] D. S. Fernandes, *Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 408; *A.*, i, 1270.

[58] G. T. Harrington and W. Crocker, *J. Agric. Res.*, 1923, **23**, 101; *A.*, i, 424.

[59] G. T. Harrington, *ibid.*, p. 117; *A.*, i, 424.

[60] E. P. Smith, *Amer. J. Bot.*, 1922, **9**, 307; *A.*, i, 1270; G. B. Ray, *J. Gen. Physiol.*, 1923, **5**, 469, 611, 623; *A.*, i, 520, 882; C. J. Lyon, *ibid.*, 1921, **8**, 458; *A.*, i, 1270.

Stoklasa [61] has studied the depression of the respiration of young pine trees by sulphur dioxide.

The loss of carbohydrate from grain during ripening has been measured by McGinnis and Taylor [62] by the amount of carbon dioxide evolved during respiration. The loss, which is considerable, reaches its maximum just before the drying off of the grain, when the moisture content is about 40 per cent.

Osmotic Phenomena : Permeability and the Absorption of Ions by Plant Cells.—In continuation of earlier work, Raber [63] has studied the mutual effects of ions on their penetration into cells of *Laminaria*, on the basis of which he attempts to explain by one general theory, based on a consideration of the charge on the membrane, the various types of antagonism met with.

Osterhout [64] and Hoagland and Davis [65] have confirmed the findings of earlier investigations, that the fresh-water alga, *Nitella*, contains most of the inorganic elements of its cell sap in a dissociated form, and that these plant cells are able to cause the movement of ions from a solution of lower concentration to one of higher concentration. Seeing that this process necessitates that the plant must do work in absorbing ions from dilute solutions, Hoagland and Davis [66] have studied the influence of light, as a source of energy, on the process, and they have shown that this absorption of ions against the concentration gradient is in fact favoured by illumination. It is concluded that light supplies the energy necessary for the transference of ions from a dilute solution into the more concentrated cell sap. They have also demonstrated that even in extremely dilute solutions one ion can markedly influence the absorption of another, as instanced by the depressing effect of chlorine-ions on the absorption of nitrate-ions. Osterhout has suggested that effects of antagonism may be relatively unimportant in very dilute solutions. According to this investigator antagonism is defined as follows : " When toxic substances act as antidotes to each other, this action is called antagonism." [67] According to this definition, it would not be strictly correct to describe the above

[61] J. Stoklasa (with J. Sebor, V. Zdobnický, and V. Nekola), *Biochem. Z.*, 1923, **136**, 306; *A.*, i, 521.

[62] F. W. McGinnis and G. S. Taylor, *J. Agric. Res.*, 1923, **24**, 1041; *A.*, i, 1164.

[63] O. L. Raber, *Proc. Nat. Acad. Sci.*, 1917, **3**, 682; from *Physiol. Abstr.*, 1923, **8**, 315; *A.*, i, 1274; *The Botan. Gazette*, 1923, **75**, 298; from *Physiol. Abstr.*, 1923, **8**, 314; *A.*, i, 1273.

[64] W. J. V. Osterhout, *J. Gen. Physiol.*, 1922, **5**, 225; *A.*, i, 76.

[65] D. R. Hoagland and A. R. Davis, *ibid.*, 1923, **5**, 629; *A.*, i, 882.

[66] *Idem, ibid.*, 1923, **6**, 47; *A.*, i, 1272.

[67] W. J. V. Osterhout, *Science*, 1916, **44**, 318.

observations made by Hoagland and Davis as antagonism, but from the point of view of nutrition and the general metabolism of the plant the latter phenomena are also of very great interest, and their interpretation provides a fruitful field of research for the plant physiologist.[68]

The nature of the membrane must be taken into account in all investigations of this sort, and in this connexion the recent work of Loeb with regard to ion–protein relations is probably significant, especially with regard to the marked influence of hydrogen-ion concentration on permeability.

On the basis of experiments on the absorption of water and acid dyes by potato tissue, Robbins [69] advances the hypothesis that an ampholyte, possibly a protein, plays the chief part in these processes, and that its isoelectric point is in the vicinity of p_{H} 6·0. The bearing of this hypothesis on theories of permeability of the plasma membrane is discussed.

Plant Constituents and Products.

Inorganic Constituents.—McHargue [70] has found that the manganese content of the seeds of grasses and cereals is roughly equal to that of iron, but in leguminous plants there is far more iron than manganese. Schmidt and his co-workers have developed a method for the removal of incrustive substances from plant tissues, depending on the use of 6 per cent. aqueous chloride dioxide solution.[71] According to Freundler, Laurent, and Ménager, iodine may be regarded as of importance in *Laminaria* in connexion with the storage of reserve energy material.[71a]

Organic Plant Products.—In this section the occurrence of organic substances in plants, and their constitution, are considered only so far as they appear likely to give an insight into their mode of formation in the plant. For references to the large number of papers dealing solely with the occurrence of plant products, the index to the *Journal* should be consulted, whilst work on the constitution of plant products is dealt with in the Reports on Organic Chemistry.

Carbohydrates.—Ling and Nanji [72] have made an important

[68] Other papers on permeability: S. Prát, *Biochem. Z.*, 1923, **136**, 366; *A.*, i, 636; M. M. Brooks, *Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 39, 384; U.S. Public Health Reports, 1923, 1449, 1470; *A.*, i, 1273; W. Seifriz, *Ann. Bot.*, 1923, **37**, 489; *A.*, i, 1043. See also Newton, *loc. cit.*

[69] W. J. Robins, *Amer. J. Bot.*, 1923, **10**, 412.

[70] J. S. McHargue, *J. Agric. Res.*, 1923, **23**, 395; *A.*, i, 635.

[71] E. Schmidt and A. Mierster, *Ber.*, 1923, **56**, [*B*], 1438; E. Schmidt, E. Geisler, P. Arndt, and F. Ihlow, *ibid.*, p. 23; *A.*, i, 274.

[71a] P. Freundler, (Mlle) Laurent, and (Mlle) Ménager, *Bull. Soc. chim.*, 1922, [iv], **31**, 1341; *A.*, i, 276.

[72] A. R. Ling and D. R. Nanji, *T.*, 1923, **123**, 2666.

contribution to the problem of the constitution of starch, which is referred to here owing to its important bearing on many plant problems, although its discussion is outside the scope of this Report. Ling has also applied his method for the estimation of starch, to potatoes.[73] Verhulst, Peterson, and Fred [74] suggest, from an examination of the maize plant, that pentosans are produced from starch. Tutin [75] advances evidence against the existence of "protopectin," which thus, in his opinion, cannot be the cause of the hardness of unripe fruit. Buston and Schryver [76] have isolated a new triose from cabbage leaves, to which they assign the constitution $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}O{\cdot}CH_2{\cdot}OH$; they discuss the possible relation of this substance to anthocyanin formation.

Pigments.—Wlodek [77] has studied the influence of light and of fertilisers on the chlorophyll coefficient (ratio of chlorophyll *a* to chlorophyll *b*) in the potato, sugar beet, and in *Iris germanica*. It is interesting to note that the coefficient falls, corresponding to an increase in chlorophyll *b*, which is richer in oxygen than chlorophyll *a*, during daylight, that is, during a time when, owing to photosynthesis, oxygen is being liberated; at night, when oxygen is being used up by respiration, the proportion of chlorophyll *b* falls, that of chlorophyll *a*, with less oxygen, rises. Lack of potassium tends to diminish the amount of chlorophyll *b*, and to increase that of chlorophyll *a*, whilst lack of nitrogen has the reverse effect.

Noack [78] has shown that the equilibrium in green plants between flavonols and their reduction products, the anthocyanins, is normally on the side of flavonol. If, however, assimilation is inhibited by injury to the chloroplasts or otherwise, anthocyanin is formed from flavonols.

Alkaloids.—Annet and Bose [79] have found that the meconic acid content of Indian opium is roughly equivalent to that of the total alkaloids present; they conclude that the latter exist in the latex

[73] A. R. Ling and W. J. Price, *J. Inst. Brewing*, 1923, **29**, 732; *A.*, 1922, ii, 879; 1923, ii, 702. Other papers on the subject are by Franz Tempus, *Naturprodukte*, 1923, 52; G. P. Walton and Mayne, R. Coe, *J. Agric. Res.*, 1923, **12**, 995; *A.*, ii, 588.

[74] J. H. Verhulst, W. H. Peterson, and E. B. Fred, *J. Agric. Res.*, 1923, **23**, 655; *A.*, i, 638.

[75] F. Tutin, *Biochem. J.*, 1923, **17**, 510; *A.*, i, 1162.

[76] H. W. Buston and S. B. Schryver, *ibid.*, p. 470; *A.*, i, 1062.

[77] J. Wlodek, *Bull. Acad. polonaise Sci. let., Classe Sci. Math. Nat.*, 1920, [*B*], 19; 1921, [*B*], 143; *A.*, i, 1160, 1161.

[78] K. Noack, *Z. Bot.*, 1922, **14**, 1; from *Chem. Zentr.*, 1923, I, 964; *A.*, i, 937.

[79] H. E. Annett and M. N. Bose, *Mem. Dept. Agric. India*, 1922, **6**, 215; *A.*, i, 358.

wholly as meconates, the sulphates present being those of mineral bases.

Plant Enzymes.—Without here dealing with the more general question of the mode of action of plant enzymes, papers published during the year on their occurrence in plants may be referred to. Ling and Nanji [80] have demonstrated the presence of maltase, not only in malt, whether green or kilned, but also in ungerminated barley, although in this case the enzyme is insoluble and its presence can be demonstrated only by employing the ground barley instead of an extract. As maltase is destroyed by alcohol, it is not present in diastase preparations obtained by the addition of alcohol to aqueous extracts of malt.

Sjöberg [81] found a very marked increase in amylase content of seeds during ripening; he has also noted that the amylase activity of plants is usually greatest in the young leaves. Oparin [82] states that increased partial pressure of oxygen is without effect on the formation of enzymes during the germination of wheat grains, with the exception of oxygenase, which is inhibited. Conversely, replacement of oxygen by an inert gas such as hydrogen is inimical to all the enzymes except oxygenase.

Goris and Costy [83] have studied the distribution of urease in twelve species of fungi. In all cases, the hymenium contained the greatest proportion of the enzyme. Kato [84] claims to have shown that urease consists of two constituents, one stable and the other labile to heat.

According to Palladin and Manskaja [85] peroxydase occurs in plant cells not only in the cell sap, but also associated with the protoplast. Gallager [86] has demonstrated the presence in the potato of an autoxidisable substance which appears to be akin to lecithin, and is concluded to be the so-called oxygenase of the potato. In this connexion, it is interesting to note that Raper and Wormall [87] have shown that the acceleration of potato tyrosinase by the addition of boiled potato juice is due, not to the inorganic constituents, but to some organic activator. Annet [88] has found

[80] A. R. Ling and D. R. Nanji, *Biochem. J.*, 1923, **17**, 593; *A.*, i, 1162. See also L. Maquenne, *Compt. rend.*, 1923, **176**, 804; *A.*, i, 442.

[81] K. Sjöberg, *Biochem. Z.*, 1922, **133**, 218; *A.*, i, 275.

[82] A. Oparin, *ibid.*, **134**, 190; *A.*, i, 425.

[83] A. Goris and P. Costy, *Compt. rend.*, 1922, **175**, 998; 1923, **176**, 412; *A.*, 1922, i, 1220; *A.*, i, 171, 405.

[84] N. Katô, *Biochem. Z.*, 1923, **136**, 498; **139**, 352; *A.*, i, 622, 1034.

[85] W. Palladin and (Frl.) S. Manskaja, *Biochem. Z.*, 1923, **135**, 142; *A.*, i, 427.

[86] P. H. Gallagher, *Biochem. J.*, 1923, **17**, 515; *A.*, i, 1159.

[87] H. S. Raper and A. Wormall, *ibid.*, p. 454; *A.*, i, 1146.

[88] H. E. Annett, *ibid.*, 1922, **16**, 763; *A.*, i, 281.

an oxydase in the latex of the Indian opium poppy, and suggests that the loss of morphine in dry opium powder on storage may be due to the action of oxidising enzymes.

Němec and Duchon [89] have brought forward further evidence in support of their view that the vitality of seeds is correlated with their catalase activity.

Vitamins.—Coward [90] has further studied the factors controlling the formation of vitamin-*A* in green plants. She finds that light is essential, but not ultra-violet light; the formation of the vitamin occurs in artificial light as well as in daylight. The presence of carbon dioxide and of oxygen in the surrounding atmosphere, of chlorophyll in the plant, and of more than traces of calcium in the nutrient solution, does not appear to be necessary, but the process is inhibited by chloroform. H. J. Page.

[89] A. Němec and F. Duchon, *Ann. Sci. Agron.*, 1923, **40**, 121.
[90] K. H. Coward, *Biochem. J.*, 1923, **17**, 134; *A.*, i, 521.

CRYSTALLOGRAPHY.

The scientific study of crystals and minerals has always been a subject which contributed to and borrowed from many neighbouring sciences, and perhaps the credit and debit have for a long time nearly balanced. But in the last decade, owing to the introduction of the method of *X*-rays, crystallography has made such rapid strides and assumed such outstanding importance that its contributions to allied sciences are undoubtedly beginning to outweigh its debt. The last few years have witnessed the practical confirmation of the theoretical basis of crystallography, and, from this point of view, the year 1923 is noteworthy in having brought forward a large mass of useful evidence which has definitely made for solid progress. The science has now attained a position from which it can speak with authority.

Structure Theory.

Thirty years ago, the geometrical theory of crystallography found its final expression, and the labours of Fedorov, Schoenflies, and Barlow had succeeded in establishing that there are 230 types of homogeneous structure to which the ultimate structural details of crystals must conform. Twenty more years elapsed before there appeared a method capable of putting this purely geometrical theory to the practical test. Naturally, the first workers in the *X*-ray analysis of crystals were physicists. These pioneers were wise in refraining from plunging deeply into a theory and nomenclature which are nothing if not confusing to the uninitiated, and the first results gave the relative positions of the atoms and molecules in simple terms familiar to all. This procedure was undoubtedly the safest plan. It was this simple statement of results in terms of positions of atoms and molecules which showed that theoretical crystallographers were on the right track and which indicated that the geometrical theory could be adopted unreservedly. The work of Fedorov, Schoenflies, and Barlow has been justified, and it is satisfactory to know that there is at hand a complete theory, tested and confirmed again and again, which can be used fearlessly and yet in perfect harmony with a rapidly developing technique.

In its essentials, the geometrical theory of crystallography treats of systems of operations whereby infinite systems of points may

be brought to coincidence. From the physical point of view, these points, in the most general case, are simply corresponding points of asymmetric bodies with definite relative positions and orientations. Of the structure of the ultimate asymmetric bodies the theory takes no cognisance, and, of course, it is unaffected by the substitution of a body of n-fold symmetry for n-asymmetric bodies of suitable positions and orientations.

As was pointed out last year by Sir Wm. Bragg [1] and G. Shearer,[2] it seems that Nature, for these structural bodies, has made use of the substance, if not always the form, of the individual chemical molecules. There is nothing in the theory against the use of polymerides of chemical molecules, but experiment has shown that, in the case of organic and non-ionised substances in general, the simple chemical molecules are the ultimate structural bodies. The combination of this fact with the theory of space-groups leads at once to a knowledge of the symmetry of the molecule in the crystalline state. This is a natural consequence of the fact that the theory is unaffected by the replacement of n-asymmetric bodies of suitable positions and orientations by another body of n-fold symmetry. T. V. Barker [3] has pointed out that E. von Fedorov in 1912 [4] made similar proposals, and acknowledgment is due to both for this. The definite advance is the recognition of the nature of the structural bodies to which the rules can be applied, for, in reality, the latter have existed for thirty years, and are contained implicitly in the work of Fedorov, Schoenflies, and Barlow.

The rule that the symmetry number of the molecules is obtained by dividing the symmetry number of the class by the number of molecules per (true) unit cell requires modification when we consider the case of ionised molecules. There is little doubt that simple chemical molecules go to build up crystals, but often in a crystal, just as in a solution, it is impossible to associate any definite atomic group with the chemical molecule, for the simple reason that the features of the ionised solution are preserved in what we may call the ionised crystal. There is an equilibrium distribution of positive and negative ions, and, as far as we can see at present, the ordinary chemical forces are indistinguishable from the cohesive forces. It is impossible to describe any definite ion as belonging to another of opposite sign. In such circumstances, it is clear that the unmodified rule does not apply, and it is necessary to fall back on the fundamental concept of the theory of space-groups, that of systems of coincidence movements

[1] *T.*, 1922, **121**, 2766. [2] *Proc. Physical Soc.*, 1923, **35**, (ii), Feb.
[3] *Nature*, 1923, **111**, 632. [4] *Z. Kryst. Min.*, 1912, **52**, 22.

or symmetry operations. For instance, in a case like that of cæsium chloride, in which there is a cæsium atom at each corner of a cube and a chlorine atom in the middle, there is the substance of one chemical molecule per cell and the whole structure has (probably) full cubic (48-fold) symmetry. We cannot point to a definite chemical molecule, and even if we could, it would clearly possess less than the 48-fold symmetry which the rule demands. But yet the complete structure extended indefinitely is obviously subject to one (O_h') of the 48-fold systems of coincidence operations as defined by the theory of space-groups. The symmetry in this case cannot be approached from a less restricted point of view. The ultimate structural body to which the rule now applies is a positive ion surrounded by its shell of eight negative ions, or a negative ion surrounded by its shell of eight positive ions. We cannot in fairness consider anything smaller because of the impossibility of stating definitely to which of the eight negative ions the included positive ion belongs. When considered from this point of view, the case is analogous to that of organic molecules.

The method by which R. W. G. Wyckoff [5] has analysed a large number of crystals is more convenient for the discussion of those crystals in which the chemical molecule is indistinguishable, since it is the analytical expression of the theory of space-groups. Wyckoff uses the co-ordinates of the equivalent points of the system, so specialised that certain sets coincide on elements of symmetry. By this means the number of equivalent points, starting from the most general case, is reduced step by step, whereupon it is found that for each number of equivalent points alternative cases present themselves. For details of this method, which is largely used in America, reference should be made to Wyckoff's book [5] and to various papers published in American scientific journals. A simple example will here suffice, C_s', the simplest type of monoclinic domatic crystal. Two asymmetric bodies which are the reflections of each other are required to produce this symmetry. If, however, it were found that the unit cell contained one molecule of a compound AB, it would not necessarily follow that the AB molecule was symmetrical about a plane (as the unmodified rule would suggest); for when we reduce, by coincidence in a symmetry plane, the two equivalent points of the group C_s' to one equivalent point, *two* cases are derived, (*a*) in which AB lies in planes parallel to the symmetry plane (010), and (*b*) in which A lies in planes (010) while B lies in planes halfway between the A-planes. This, in its simplest form, is the

[5] "The Analytical Expression of the Results of the Theory of Space-Groups."—Carnegie Inst. of Washington, Oct., 1922.

method used by Wyckoff and his followers. It is the complete analytical expression of the geometrical theory of crystallography.

T. V. Barker [6] and J. W. Evans [7] have raised objections to the considerations put forward last year by Sir Wm. Bragg [8] and G. Shearer,[9] but, when viewed from the point of view of the theory, the rules suggested cannot be refuted. On the other hand, Barker's contention that the symmetry of the molecule does not necessarily reveal itself in the symmetry of the structure must be considered if only with a view to remove all misunderstanding. It has never been claimed that the symmetry of a molecule in a crystal is identical with the symmetry of that molecule in solution or in the free state. Probably the latter symmetry is the greater of the two, but, in any case, a simple example of dimorphism like that of calcite and aragonite shows that molecular symmetry is by no means unchangeable. In calcite, the carbonate group is symmetrical about a triad axis, whereas in aragonite it is not. Nevertheless, it must be remembered that it requires very little distortion of a molecule to destroy its symmetry, and that it is not at all likely that the act of crystallisation involves great distortion. We must accordingly believe that, although the chemical molecule is not necessarily identical with the crystal molecule, it is not very far removed from it.

The molecule as it exists in the crystal is part of the structure, and, by the theory of space-groups, its symmetry *in the crystal* is part of the symmetry of the structure. This much is perfectly clear, when there is no misunderstanding as to what is meant by the symmetry in the crystal. The symmetry of the molecule in the crystal is a property which is perceived only indirectly, that is, *via* the symmetry of the structure as a whole. It is merely the symmetry of the immediate environment of the molecule, or, in other words, the symmetry of the points of contact with its neighbours. Whether this can be considered as extending right down into the heart of the molecule is another question. In the case of crystals of elements, diamond, for instance, it is not likely that it extends any deeper than the outer shell of electrons, but since it is probable that chemical molecules are built up from atoms by the agency of these outer electrons, it is difficult to believe that a crystal molecule with symmetrically arranged environment may yet be completely asymmetric in the body of the molecule. Such a thing is not impossible, of course, but, physically speaking, it appears highly improbable.

Recently there have appeared several papers discussing the

[6] *Nature*, 1923, **111**, 632; **112**, 96. [7] *Ibid.*, 1923, **111**, 740.
[8] *T.*, 1922, **121**, 2766. [9] *Proc. Physical Soc.*, 1923, **35**, (ii), Feb.

question as to whether the criteria which have hitherto been accepted in crystallography are really safe guides to the true symmetry of the structure. These criteria are such properties as facial development, etched figures, piezo- and pyro-electric effects, etc., and before the advent of *X*-ray analysis a crystal was assigned to one of the thirty-two classes on the strength of such evidence alone. And there is no doubt that in the great majority of cases the conclusion is correct. But now that so many crystal structures have been analysed more or less completely, discrepancies have been found. In some cases, the symmetry of the structure as deduced from *X*-ray analysis is different from that obtained from the ordinary crystallographic data. Cases in point are potassium chloride and ammonium chloride, both of which have hitherto been described as cubic holoaxial (class 29). The structure of potassium chloride is definitely known and to all appearances it is cubic holosymmetric (class 32), while, although the structure of ammonium chloride is not known with absolute certainty, this much is quite clear, that it belongs to one of the cubic classes which are symmetrical about *planes* as well as axes, probably the hexakis tetrahedral class, or if not that, then the holosymmetric class. An interesting paper on the subject has been contributed by E. T. Wherry,[10] and the case of ammonium chloride has been discussed by R. W. G. Wyckoff.[11] Apparently another example is afforded by $CaS_2O_3,6H_2O$,[12] which has always been supposed to belong to the anorthic asymmetric class (1). The unit cell of this crystal contains *two* molecules which, by analogy with other anorthic crystals and organic crystals in general, are the inversions of each other, that is, the crystal really belongs to the anorthic pinakoidal class (2). This conclusion is not absolutely certain, as it is based on the hypothesis that single molecules are used instead of polymerides (a rule which has been found to hold in all other cases examined), but it must be allowed that the *X*-ray evidence is strongly against the original crystallographic conclusion. We can get out of the difficulty in the case of potassium chloride by assuming that both the potassium- and the chlorine-ions possess only cubic holoaxial symmetry, and for $CaS_2O_3,6H_2O$ we can say that a two-molecule polymeride has been used, but the case of ammonium chloride is not so easily dismissed and at present no solution of the problem is forthcoming. T. V. Barker [13] has written at some length to protest against this tendency to ignore crystallographic evidence, but he confesses his inability to explain the divergence of ammonium chloride. For the rest, he suggests

[10] *Amer. J. Science*, Sept., 1922.
[11] *Ibid.*, 1922, [v], **4**, 469.
[12] W. T. Astbury, *Nature*, 1923, **112**, 53.
[13] *Ibid.*, p. 502.

that the periodicity in the crystal structure that is revealed by *X*-rays is not necessarily the *true* periodicity of the structure, since (*sic*) it is generally accepted that the outer electrons do not appreciably scatter the *X*-rays. There is no denying that what Barker suggests may be true, but, as Sir Wm. Bragg [14] stated in his reply, we must not forget that in diamond at least, the conclusion is that the outer electrons *do* scatter the rays, or how else can we explain the observed tetrahedral symmetry of the atom? Such evidence points to the fact that *X*-rays do detect the true periodicity and that for an explanation of the anomaly of ammonium chloride and other crystals (diamond itself is one) we must look in other directions. The reason may be that the surface conditions of crystals are not always the same as those holding within the body, but for want of a more definite answer, the question for the present must be left *sub judice*.

It has been mentioned above that the early workers in crystal analysis by *X*-rays did not make use of the nomenclature of the theory of space-groups. This procedure has been condemned by R. W. G. Wyckoff [15] in his "Survey of Existing Crystal Structure Data," and unjust statements have been made. These have been answered elsewhere.[16] Wyckoff has also published a paper condemning the hypothesis of constant atomic radii,[17] but here again it must be maintained that in the original paper on atomic radii [18] no such rigid doctrine was ever advanced. It was pointed out that there is an approximate additive law which may be helpful in the study of complex structures, and that the curve obtained by plotting the "radii" characteristic of the atoms resembles Lothar Meyer's curve of atomic volumes and is susceptible of a ready explanation in terms of the Lewis-Langmuir theory of chemical combination. Although characteristic numbers were calculated for most of the elements, strict observance of these was never advocated. Indeed, it is not at all likely that the same atom in different environment will occupy precisely the same space. Wyckoff has recalculated the "atomic radii," starting from different points, and he naturally finds large discrepancies. To quote from his paper, "these data conform to the rule that in isomorphous crystals composed of only two kinds of atoms the interatomic distances have additive properties which can be illustrated through a summing up of 'atomic radii.' The data also show that for compounds of different crystal structures in

[14] W. T. Astbury, *Nature*, 1923, **112**, 618.
[15] *J. Franklin Inst.*, 1923, **195**, 183, 349, 531.
[16] Sir W. H. Bragg, *ibid.*, 1923, **196**, 675.
[17] *Proc. Nat. Acad. Sci.*, 1923, **9**, 2, 33.
[18] W. L. Bragg, *Phil. Mag.*, 1920, [vi], **40**, 169.

which atomic environments are different, the interatomic distances likewise are unlike. Where the changes of environment are relatively small, this change in interatomic distance may be almost negligible; in other cases, it amounts to several tenths of an Ångstrom unit."

This is no doubt a correct conclusion, but when we remember that the real difficulty of crystal analysis begins where space-group theory ends and that we are far from being able to interpret correctly the various intensities of reflection, the good points of the hypothesis of constant atomic radii may not be so lightly discarded. In organic crystals especially is it useful (see below), for there is much evidence to show that 1·5 Å.U. is nearly always a good working value for the "atomic diameter" of carbon, and, in fact, in chain-compounds the influence of hydrogen appears negligible. Long rows of successive carbon atoms conform in a remarkable manner with the carbon "diameter" found from diamond. T. W. Richards [19] has contributed a theoretical paper on the subject of atomic radii. Like Wyckoff, he points out the inaccuracy of the hypothesis of constant atomic radii, since atoms are subject to different "internal pressures" (defined as the pressures due to the forces of affinity), in different chemical combinations, and their dimensions depend on this and on the compressibilities of the elements concerned.

An interesting paper on a related subject, that of structure and isomorphism in crystals, has been contributed by Wyckoff to the *American Mineralogist*.[20] He states that "no general and exact statement of the connexion between isomorphism and atomic arrangement can be made at the present time." The discussion arose out of two recent papers on isomorphism,[21, 22] and it is fortunate that this has happened, since a summary of the conclusions to be drawn from crystal analysis is a welcome addition to the study of the subject. Isomorphous crystals will not in general have *identical* crystal structures, for even in the simple cases so far examined the variable parameters which describe the atomic positions have not been found to have identical values. H. S. Washington and Wyckoff suggest the use of the term "homeotaxial" for crystals which are chemically alike, with the same type of atomic arrangements, and in which the respective distributions of atoms are so nearly similar that they are isomorphous in the usual sense. Examples of such homeotaxial

[19] *Wash. Nat. Acad. Sci.*, 1923, **9**, 73; *J. Amer. Chem. Soc.*, 1923, **45**, 422.
[20] 1923, **8**, May.
[21] E. T. Wherry, *Amer. Mineralogist*, 1923, **8**, 1.
[22] F. Zambonini [H. S. Washington], *ibid.*, p. 81; *Rend. Accad. Lincei*, 1922, **31**, 295.

crystals are pyrites and hauerite, but not zinc blende and galena. All homeotaxial crystals are isomorphous in its widest sense, but we cannot say that all isomorphous crystals are homeotaxial. We do not at present know enough about the atomic arrangements in complicated crystals to justify a generalisation as to how far we may depart from complete identity and yet retain isomorphism. By choosing for discussion such favourable cases as are offered by the alkali and alkaline-earth metals, we have overlooked the numerous cases of atomic replacement which should be possible, but have not been found. The following table (taken from Wyckoff's paper) will bring home how difficult it is at the present time to prophesy in advance of experiment anything about probable atomic arrangements.

TABLE I.

NaCl grouping.		NH_4Cl grouping.	Cubic ZnS grouping.	ZnO grouping.
LiX	NaX	CsCl	CuCl	AgI
KX	RbX	CsBr	CuBr	CdS
CsF	NH_4I	CsI	CuI	ZnS
MgO	CaO	TlCl	ZnS	ZnO
CdO	AgCl	NH_4Cl		
NiO	AgBr	NH_4Br		
CaS	MnS			

[X represents any of the halogen atoms.]

There is much evidence to show that neither homeotaxis nor isomorphism is determined *primarily* by the atomic sizes. Crystals with such widely different molecular volumes as lithium fluoride and cæsium fluoride are completely homeotaxial, as are also the potassium and cæsium alums. And besides, as Wyckoff points out, if the atomic sizes be the basic criterion in a solid solution of albite and anorthite, why does not a similar replacement (that of Na and Si for Ca and Al) hold in the case of the cubic garnets? Yet even although the sums of the valencies also balance, no cubic garnets of this sort are found. Although no doubt isomorphous replacement is unlikely if the respective sizes of the atoms involved in the substitution are not very similar, the results of crystal analysis do not justify the idea that this is the principal determining factor in such replacements.

Structure of Alloys and Metals.

Early in the present year E. C. Bain [23] gave an account of an *X*-ray examination of a large number of alloys. He investigated solid solutions of tin, zinc, manganese, and aluminium in copper, cadmium and zinc in silver, and tungsten, molybdenum, chromium,

[23] *Chem. and Met. Eng.*, Jan. 3rd and 10th, 1923.

and manganese in iron. The investigations of Bain and of his co-workers have the merit of being largely pioneer work with respect to the particular cases examined and as such are worthy of special consideration, in spite of the fact that the results cannot be accepted without reserve. Bain's results in these two papers suffer from the defect—a serious one to metallurgists—that results are given with insufficient detail or without statement of experimental conditions. Furthermore, they cannot always claim to be in good agreement with confirmed thermal and microscopical investigations. Some of the work has already been repeated more satisfactorily elsewhere (see below), but the details of the remainder will be summarised. *Cu–Zn* :—Thirty per cent. Zn changes edge of face-centred Cu from 3·60 Å.U. to 3·68 Å.U. (α-brass). The ranges of the brasses in these experiments do not correspond accurately with the ranges given by thermal and microscopical investigations. The brasses have been examined thoroughly by Owen and Preston (below). *Cu–Sn* :—Five per cent of Sn atoms expands the side of Cu from 3·60 to 3·655, which is less than would be expected from a consideration of the respective atomic volumes. *Cu–Al* :—18·8 per cent. Al stretches Cu from 3·60 to 3·633, again less than expectation. (These alloys have been studied in detail by Owen and Preston.) *Cu–Mn* :—$33\frac{1}{3}$ per cent. Mn stretches Cu from 3·60 to 3·615 : usually described as completely miscible, but not so according to Bain's results. *Ag–Cd* :—Ag saturated with Cd increases side by 1·1 per cent. (less than expected). *Ag–Zn* :—The edge is in this case decreased from 4·06 to 4·005 Å.U. (more than would be expected). *Fe–Cr* :—No measurable distortion, as would be expected. *W–Fe and Mo–Fe* :—Both form compounds (WFe and MoFe) of a hexagonal type not yet elucidated. Fe dissolves a little W or Mo without measurable change, whilst very little, if any, Fe can be dissolved by W or Mo without the formation of the compound. *Fe–Mn* :—Up to 30 per cent. Mn preserves the body-centred Fe, up to 60 per cent. the face-centred Fe. Above 60 per cent. gives (unknown) Mn lattice distorted by Fe. *Fe–Ni* :—Contains two types, (*a*) Ni dissolved in body-centred Fe and (*b*) Fe dissolved in face-centred Ni. These exist side by side over a great range. According to *X*-rays, it is not quite true that Fe and Ni are miscible in all proportions. *Cu–Au, Cu–Ni, Au-Ag* are truly miscible (face-centred cubes). *Mo–W* :—Similar to Ag–Au except that it is body-centred.

From the above results Bain draws the conclusion that when large and small atoms pack in a common lattice, they pack more closely than would be expected, whilst unlike atoms of about the same size do not show attraction or compression to any extent.

Bain also claims, in a very few cases, to have obtained conclusive evidence of the existence of binary structures in which the atomic arrangement is not at random but really symmetrical, for example, 25 *A* : 75 *B* can give, according to Bain, besides the lines of the face-centred cube, the lines of the simple cube also. This evidence is offered in support of the chemical and electro-chemical work of Tammann, which demands for explanation the existence of such structures.

More recently than Bain's work, an account has been given, with abundant detail, of a careful *X*-ray investigation of various alloys carried out by E. A. Owen and G. D. Preston [24] at the National Physical Laboratory. These workers used the Bragg ionisation spectrometer after the manner described in an earlier paper.[25] Their results, in the cases examined, confirm the "substitutional" hypothesis of alloy structure advanced by W. Rosenhain,[26] that is, they show that solid solutions of a metal *B* in a metal *A* are built on the same space-lattice as crystals of pure *A*, with the difference that a certain number of atoms of *A* are replaced by atoms of *B*. The substitution of *B* atoms for *A* atoms is accompanied by a slight distortion of the *A* lattice in the neighbourhood of the *B* atoms, to an extent depending on the relative sizes of the two atoms. An alternative hypothesis is that the *B* atoms are received into the interstices between the *A* atoms (the work of Westgren and Phragmen indicates such a structure for steel), but in the cases examined by Owen and Preston this is certainly inapplicable. From the distortion and density changes, when these are not inappreciable, it is easy to decide between the two hypotheses. The work will now be summarised.

Al–Cu Alloys rich in Cu :—Alloys containing 2, 4, 6, and 8 per cent. by weight of Al were examined. For 8 per cent. Al, the cube side of Cu increases from 3·60 to 3·65 Å.U., and the results indicate clearly that the solution is of the substitutional type. *Al–Cu Alloys rich in Al* :—In these there is no appreciable lattice distortion, and no decision can be made between the two hypotheses. *Al–Cu Alloy containing* 30 *per cent. Cu by weight* :—It is shown that this eutectic alloy consists of $CuAl_2$ and a substance which is indistinguishable from pure Al, but which may be an Al–Cu alloy rich in Al (see above). *Structure of the compound* $CuAl_2$:—The unit cell is shown to be tetragonal with $a = 4{\cdot}28$ Å.U. and $c = 2{\cdot}40$ Å.U. The Cu-atoms lie at the corners of the cell and the Al-atoms at the centres of the side faces. Note that in this arrangement both Al centres and Cu centres are separated by 2·40 Å.U.,

[24] *Proc. Physical Soc.*, 1923, **36**, 14, 49. [25] *Idem, ibid.*, 1923, **35**, 101.
[26] *Proc. Roy. Soc.*, 1921, [*A*], **99**, 196.

a distance which is smaller than the " atomic diameters " given by the pure metals (2·86 Å.U. for Al and 2·54 Å.U. for Cu). *Structure of CuAl* :—This compound is apparently obtained from the face-centred Al lattice with such distortion that it becomes a rhomb of side 3·89 Å.U. (as against 4·05 for Al) and axial angle 94·6°. It appears to be face-centred with two molecules of CuAl per cell, with (3) planes composed alternately of Cu and Al atoms. Note that such a structure resembles the type postulated by Tammann. *Al–Mg Alloys* :—Eight per cent. Mg by weight distorts the Al lattice from side 4·05 to 4·10 Å.U., and the results agree with the substitutional hypothesis. With 92 per cent. by weight of Mg, the spectrum corresponds to the close-packed hexagonal lattice of Mg ($a = 3{\cdot}17$ Å.U. and $c = 5{\cdot}17$ Å.U.), the side being decreased to 3·15 Å.U. and the height increased to 5·23 Å.U. *Cu–Ni Alloys* :—The Ni produces a small contraction of the Cu lattice, and the results (as also those of Al–Mg alloys) are in agreement with the substitution theory.

Cu–Zn Alloys containing up to 38·7 *per cent. Zn by weight* :—These alloys gave spectra characteristic of the face-centred cubic structure of Cu. 38·7 per cent. Zn increases the side of Cu from 3·60 Å.U. to 3·696 Å.U., and the results agree with the substitutional theory. *Cu–Zn Alloy containing* 48·5 *per cent. Zn* :—This alloy lies in the region of the β-brasses, with a centred-cubic structure of side 2·950 Å.U. *The structures of the* β *and* β′ *phases are identical, and the thermal effect which occurs at* 470° *is not accompanied by a breaking up of the* β*-constituent into a mixture of* α *and* γ. *Cu–Zn Alloy containing* 67·2 *per cent. Zn* :—This alloy lies in the region of the γ-brasses. It is apparently built on a rhombohedral lattice of side 4·136 Å.U. and axial ratio 0·6495. *Cu–Zn Alloy containing* 80·1 *per cent. Zn* :—This specimen of ε-brass corresponded to a close-packed hexagonal arrangement of side 2·718 Å.U. and axial ratio 1·585, derived from that of pure Zn ($a = 2{\cdot}670$ and $c = 4{\cdot}97$ Å.U.).

The above careful *X*-ray study of the various brasses is in agreement with the constitutional diagram of Shepherd as modified by Desch and Hudson. It should be noticed that the thermal phenomenon in the β-brasses is similar to the change from α- to β-iron, that is, there is no change in crystal structure. The atomic volume curve consists very approximately of two straight lines meeting in the region of the γ-brass. In this region there is the maximum distortion from the straight line joining the atomic volumes of copper and zinc. Thus the atomic volume curve corresponds to the fact, which has been known for some time, that the hardness of the brasses increases from the copper end to the region of γ-brass

and then diminishes as we proceed to the zinc end of the series. Along one limb of the curve the crystal structure of the alloys follows the rhombohedral arrangement, and along the other the close-packed hexagonal arrangement.

Various *Heusler Alloys* have been examined by J. F. T. Young,[27] who has suggested that these alloys are solid solutions of manganese–aluminium in copper, and that the magnetic effects are associated, not with molecular or atomic groupings, but with the valency electrons.

K. Becker and F. Ebert [28] also have examined by *X*-rays certain metals, metallic compounds, alloys, and mixed crystals. If a is the side of the unit cube, they obtain the following results :—Ta, $a = 3{\cdot}32$ Å.U.; Cu_2Zn_3, $a = 4{\cdot}01$ Å.U.; mixed crystals of 96·3 per cent. Mg_4Al_3 and 3·7 per cent. Al, $a = 4{\cdot}80$ Å.U.; NiAl, $a = 2{\cdot}82$ Å.U.; Cu_3Al, $a = 3{\cdot}47$ Å.U.; Ni_6W, $a = 3{\cdot}68$ Å.U. Tantalum is body-centred cubic and thallium face-centred tetragonal ($a = 4{\cdot}75$ Å.U., $c = 5{\cdot}40$ Å.U.). It is essential that the *X*-ray study of alloys should be carried out in the closest association with thermal, microscopical, and other studies.

A system analogous to that of the alloys, the system formed by hydrogen occluded in palladium, has also been examined this year by means of *X*-rays. Mituo Yamada [29] found only a continuous displacement of the palladium lines by the occluded hydrogen, and concluded that no actual compound was formed, but only a solid solution. L. W. McKeehan [30] has drawn similar conclusions.

In the May lecture delivered to the Institute of Metals, W. Rosenhain [31] put forward certain general considerations arising out of the work of Owen and Preston. As mentioned above, this work is definitely in favour of the substitutional theory of alloy structure, and Rosenhain points out how it follows from this and the conception of a limiting atomic displacement in the lattice that great distortion is associated with low solubility and increased hardness. Similarly, it is the hard metals, for example, iron, nickel, cobalt, manganese, chromium, tungsten, and molybdenum, which form long series of solid solutions, since in them, because of their hardness, the distortion is *not* localised and the limiting parameter is not overstepped. In the soft metals, lead and tin, practically no solid solutions are formed. In a precisely analogous manner, the distortion existing in solid solutions, because it aids or opposes the break-up of a lattice by heat, lowers or raises the freezing point and causes that temperature difference which is observed between

[27] *Phil. Mag.*, 1923, [vi], **46**, 291.
[28] *Z. Physik*, 1923, **16**, 165.
[29] *Phil. Mag.*, 1923, [vi], **45**, 241.
[30] *Physical Rev.*, 1923, [ii], **21**, 334.
[31] *Inst. of Metals*, 13th May Lecture, 1923.

the beginning and the end of freezing and melting of alloys. Rosenhain also mentions the large heat absorption that occurs when metals are made amorphous by stress, and shows that metals, and crystals in general, which are plastic should (as they do) exhibit the phenomenon of diffusion. Electrical conductivity and "superconductivity" also are dealt with from the same point of view. The irregularities in the rows of atoms decrease the conductivity and temperature coefficients of alloys as compared with those of the pure metals: similarly for elastic-hysteresis and fatigue.

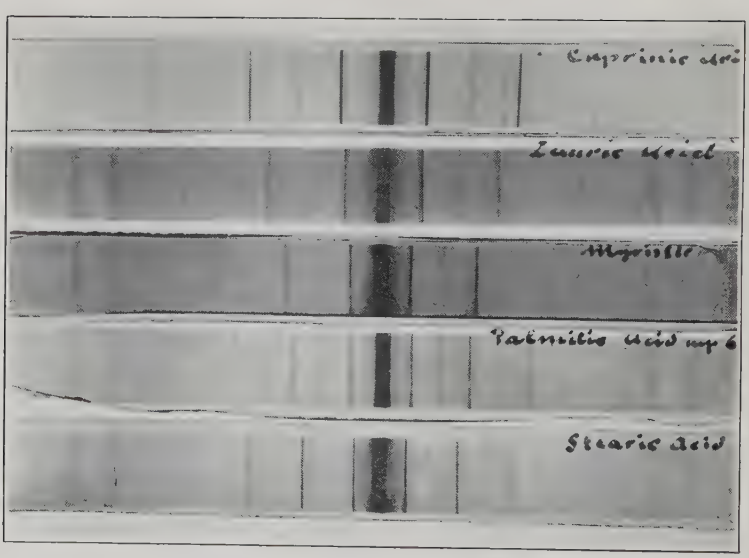
A brief mention must now be made of this year's Bakerian Lecture to the Royal Society.[32] The subject of distortion and slip-planes in metals and crystals in general is of extreme interest to the mathematician, crystallographer, and metallurgist alike, but the lecture is too mathematical to lend itself to abstraction. Prof. G. I. Taylor and Miss C. F. Elam discuss the distortion of an aluminium crystal under tensile stress and show from a study of the surface slip-lines that the planes of slip are parallel to the face (111). Prof. A. W. Porter[33] has pointed out that the phenomenon was observed ten years ago by Baker and Andrade, who showed that sodium and potassium cylinders when stretched contracted laterally so as to lead to an approximately elliptical section, and when they broke they did so at a chisel edge. The surfaces were marked with a double set of slip-lines. H. Mark and M. Polányi[34] have also been studying the phenomenon by the aid of *X*-rays. Last year they examined zinc crystals and now find analogous results for white tin. According to these authors, white tin crystallises in the ditetragonal bipyramidal class, space-group D_{4h}^{19}. The unit cell is body-centred and its horizontal axes are taken at 45° to the crystallographic axes. Its dimensions are $a = 5{\cdot}84$ Å.U., $c = 3{\cdot}15$ Å.U. There are four atoms in the cell, the co-ordinates of which are (000), ($o\,a/2\,c/4$), ($a/2\,o\,3c/4$), ($a/2\,a/2\,c/2$). Slipping was found to take place parallel to the (110) and (100) planes, the former occurring the more frequently.

Structure of Long-chain Compounds.

The *X*-ray investigation of long-chain organic compounds has been one of the most interesting and important researches of the year. It supplements and confirms the more indirect but highly ingenious work of Langmuir, Adam, and others on the dimensions of unimolecular films, and justifies hypotheses which have been held by chemists for a long time. The first observation of a long spacing (43·5 Å.U. from sodium oleate) was made by De Broglie

[32] *Proc. Roy. Soc.*, 1923, [*A*], **102**, 643. [33] *Nature*, 1923, **111**, 362.
[34] *Z. Physik*, 1923, **18**, 75.

PLATE I.



[*To face Annual Reports, p.* 243.]

and Friedel.[35] Soon after, S. H. Piper and E. N. Grindley[36] made some systematic measurements of the *X*-ray reflections to be obtained from sodium laurate (ten CH_2 groups), myristate (twelve CH_2 groups), and palmitate (fourteen CH_2 groups). These three salts, examined in the form of curds, gave wide spacings of 33·5, 38·5, and 43·5 Å.U., respectively, together with two other smaller spacings of 4·22, 4·18, 4·15 and 4·88, 4·9, 4·9 Å.U., respectively. The interesting fact is thus revealed that, whilst the small spacings remain fairly constant, the long spacing increases by 5 Å.U. per CH_2 group. From these results the authors conclude that, in order to harmonise with the work of Langmuir and of Adam, we must assume *two* molecules, end to end. The effective increase of length per CH_2 group would then be 1·25 Å.U., and the chain would be made up of a zig-zag arrangement of carbon atoms linked together at the tetrahedral angle. The authors also conclude that their observations accord with the "smectic condition" described by Friedel,[37] that is, the structures are not really crystalline.

The most complete and satisfactory *X*-ray examination of these elongated molecules has been carried out, independently of Piper and Grindley, by A. Müller and G. Shearer. In a paper by the former[38] are described the observations which are summarised in Table II and beautifully reproduced in Plate I. The increase per CH_2 group is approximately constant and equal to 2·0 Å.U., whilst the existence of the two small spacings, d_2 and d_3, suggests that the unit cell is a long prism which has the same cross-section for all the substances in question.

TABLE II.

Acid.	M. p.	*N*.	d_1.	d_2.	d_3.
Capric	—	10	23·2	—	—
Lauric	43—44°	12	27·0	4·11	3·68
Myristic	—	14	32·2	4·12	3·72
Palmitic	62·5°	16	34·7	4·08	3·65
Stearic	69—69·5°	18	38·7	4·05	3·62
Behenic	80·5°	22	47·8	4·10	3·66

M. p. denotes melting point and *N* the total number of carbon atoms in the chemical formula. Behenic acid is not reproduced in the plate.

The investigation is continued and discussed in two further papers delivered to the Chemical Society. Shearer[39] examined certain long-chain esters and aromatic compounds. The data for these are given in Table III.

[35] *Compt. rend.*, 1923, **176**, 738.
[36] *Proc. Physical Soc.*, 1923, **35**, 269.
[37] *Ann. Physique*, Nov., 1922.
[38] *T.*, 1923, **123**, 2043.
[39] *Ibid.*, p. 3152.

TABLE III.

Substance.	Formula.	d_1.	d_2.	d_3.
Methyl palmitate ...	$C_{15}H_{31}\cdot CO\cdot O\cdot CH_3$	22·0	4·07	3·72
Ethyl ,, ...	$C_{15}H_{31}\cdot CO\cdot O\cdot C_2H_5$	23·2	4·07	3·67
Octyl ,, ...	$C_{15}H_{31}\cdot CO\cdot O\cdot C_8H_{17}$	30·4	4·16	3·72
Cetyl ,, ...	$C_{15}H_{31}\cdot CO\cdot O\cdot C_{16}H_{33}$	40·4	4·05	3·69
Methyl stearate	$C_{17}H_{35}\cdot CO\cdot O\cdot CH_3$	24·0	4·07	3·74
Ethyl ,, ...	$C_{17}H_{35}\cdot CO\cdot O\cdot C_2H_5$	25·2	4·14	3·69
Octadecylbenzene ...	$C_{18}H_{37}\cdot C_6H_5$	49·2	—	—
p-Hexadecylphenol...	$C_{16}H_{33}\cdot C_6H_4\cdot OH$	46·5	—	—
p-Octadecylphenol ...	$C_{18}H_{37}\cdot C_6H_4\cdot OH$	51·3	—	—

These results indicate a uniform increase of 1·22 Å.U. on the ester side of the molecule as compared with the increase 2·0 Å.U. found by Müller for the fatty acids. In the third (joint) paper [40] are given the following supplementary results (Table IV), and the conclusions to be drawn from the whole are discussed.

TABLE IV.

Substance.	Formula.	d_1.	d_2.	d_3.
Undecylic acid	$C_{11}H_{22}O_2$	24·7	—	—
Pentadecylic ,, ...	$C_{15}H_{30}O_2$	36·2	4·00	3·76
Margaric ,, ...	$C_{17}H_{34}O_2$	38·2	4·05	3·77
Oleic ,, ...	$C_{18}H_{34}O_2$	36·2 (?)	—	—
Elaidic ,, ...	$C_{18}H_{34}O_2$	48·3	4·03	3·65
*iso*Oleic ,, ...	$C_{18}H_{34}O_2$	35·9	—	—
Erucic ,, ...	$C_{22}H_{42}O_2$	46·3	4·22	3·72
Brassidic ,, ...	$C_{22}H_{42}O_2$	59·9	4·25	3·72

These conclusions are of fundamental importance to chemists, and may be stated briefly as follows.

The authors argue that these long-chain compounds form *real crystals* which are all built up after a similar fashion, with the length of the molecule lying approximately perpendicular to the cleavage flakes. These latter generally lie parallel to the surface on which they crystallise out. What we may provisionally call the unit cell is a long, narrow prism of height d_1 and side dimensions d_2 and d_3. Such a cell would show only one large spacing, all the rest being small. In some of the compounds d_1 represents the length of a single molecule (the case of one molecule per cell, or, at least, one molecule between successive cleavage planes), and in others the length of two molecules, end to end and pointing in opposite directions (two molecules per cell). Thus d_2 and d_3 are approximately constant, because they represent the width of the chains, whilst d_1 varies in two observed ways: (*a*) an increase of $2\cdot0/2 = 1\cdot0$ Å.U. per CH_2 group; (*b*) an increase of 1·22 Å.U. per CH_2 group: (*a*) is exemplified by the fatty acids and other compounds containing two molecules per cell, whilst (*b*) is exemplified by the ester side of long-chain esters containing one molecule per cell.

[40] A. Müller and G. Shearer, *T.*, 1923, **123**, 3156.

The authors now consider the question, What are the possible types of carbon chains, given that the linking is always at the tetrahedral angle (that is, 109°28′, as observed in diamond), and that the continued addition of a limited number of atoms to the chain always results in a uniform increase in the length of the chain? There are several chains which satisfy these conditions. The three simplest are shown in Figs. 1, 2, and 3.

In Fig. 1 the atoms are all in one plane, and the increase per

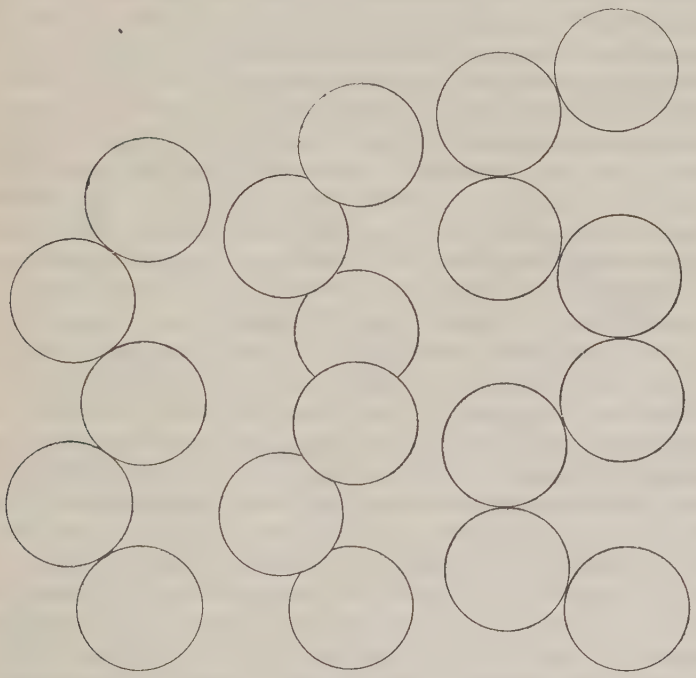


Fig. 1. Fig. 2. Fig. 3.

carbon atom, given that the carbon "diameter" is 1·5 Å.U., is 1·22 Å.U. The chain in Fig. 2 is a spiral, of which the period is three atoms. It is like the spiral of silicon atoms in quartz, and the increase per carbon atom is 1·12 Å.U. In Fig. 3 the period is four atoms and the increase is 2·0 Å.U. for *two* carbon atoms, each set of four atoms lying in a plane, but successive sets not necessarily co-planar. The chains in Figs. 1 and 3 are exemplified by the esters and fatty acids, respectively.

The above remarks outline the chief features of this new advance in chemical crystallography, but there are several other interesting points, such as the nature of "double bonds" and of *cis*- and

trans-isomerism, considered in the papers mentioned. For these reference should be made to the original discussion.

Structure of Inorganic Crystals.

In the following summary, all points of peculiar interest, especially chemical, will be indicated where need arises, and the bearing of the results on current theory briefly discussed.

Hydrazine Dihydrochloride, $N_2H_4,2HCl$.[41]—This salt crystallises in the same class and subgroup (T_h^6) as iron pyrites. There are four molecules per cell and the side of the unit cube is 7·89 Å.U. The structure is also analogous to that of the nitrates of the alkaline earths, the centres of the hydrazine groups ($N_2H_6^{++}$) replacing the centres of the metals at the corners and face-centres of the cube, and the chlorine atoms replacing the nitrate groups. In aqueous solution, the salt presumably ionises to doubly-charged (N_2H_6) groups and negative chlorine-ions. Apparently the distance between nitrogen and chlorine centres is 3·14 Å.U., and between two chlorine centres 3·96 Å.U. These results are at variance with the hypothesis of constant atomic radii.

The Alums, $R'R'''(SO_4)_2,12H_2O$.[42]—Earlier *X*-ray examination [43] of this series of double salts assigned to them the space-group T_h^2, but this recent investigation has decided in favour of T_h^6 (the iron pyrites class and group). The dimensions and the number of molecules per cell (four) are the same, and no attempt has been made completely to locate the atoms. There are, however, certain general conclusions to be drawn from these latest results. (1) All four of the oxygen atoms of the sulphate group cannot be exactly alike. Three of the oxygen atoms must be alike, but different from the fourth. (2) The twelve water molecules fall into two groups of six each. (3) The hydrogen atoms of the ammonium groups in the ammonium alum present an interesting difficulty. The only arrangement which satisfies symmetry considerations makes all five of the atoms of the ammonium group lie on a straight line, a triad axis of the crystal, and such a grouping is not chemically plausible. As a possible way out of this difficulty, Wyckoff suggests that the hydrogen atoms need not have a symmetry which conforms to that of the crystals as a whole and yet, because of the few electrons involved, be still in agreement with *X*-ray and optical data. Such a hypothesis must be approached warily; more examples are necessary before a decision can be arrived at. Wyckoff quotes the case of the alums as a particularly good example of the futility of unaided spectrometric investigation.

[41] R. W. G. Wyckoff, *Amer. J. Sci.*, 1923, **5**, 15.
[42] *Idem*, *ibid.*, p. 209; *Z. Krist.*, 1923, **57**, 595.
[43] L. Vegard and H. Schjeldemp, *Ann. Physik*, 1917, **54**, 146.

Cubical Arsenious and Antimonious Oxides, As_4O_6 *and* Sb_4O_6.[44]—The interest attaching to the determination of the structure of these two compounds has been greatly enhanced by the almost simultaneous discovery of the structure of basic glucinum acetate.[45] All three are built on the "diamond structure," space-group O_h^7. The molecules preserve their identity in the crystal and possess the 24-fold symmetry of the regular tetrahedron. We must therefore consider the arsenic and antimony atoms as associated with the four corners of a regular tetrahedron and the oxygen atoms with the six edges of the same tetrahedron. The sides of the unit cubes containing eight molecules are 11·06 Å.U. for As_4O_6 and 11·14 Å.U. for Sb_4O_6. The shortest distance between arsenic and oxygen atoms is 2·01 Å.U., and between antimony and oxygen atoms 2·22 Å.U.

Quartz, SiO_2.[46]—This crystal has been again investigated this year, but by the powder method. The author confirms the hexagonal lattice found by Bragg [47] and concludes that the molecules are obtuse-angled isosceles triangles, having an angle at the silicon atom centre of 115° 14′, and a distance between the silicon and oxygen atoms of 1·631 Å.U. The molecules are said to lie completely in the basal planes of the three interpenetrating hexagonal lattices, but such a conclusion is difficult to accept when we consider the intensities of the different orders of reflection from the basal plane. Sir Wm. Bragg has recently considered the question anew and a discussion is given in "*X*-Rays and Crystal Structure" (new edition, now in the press). If all the atoms lie in successive basal planes, as McKeehan suggests, we should expect a more or less "normal" falling-off of intensities in the successive orders of reflection from the basal plane, but actually experiment shows that the second order is abnormally large.

Cinnabar, HgS.[48]—This crystal belongs to the same crystal class as quartz, but is much more optically active. The author concludes that it belongs to Type (23—24) of Sohncke, with $c = 9{\cdot}51$ Å.U. and $a = 4{\cdot}15$ Å.U. The reflections from the basal plane (second order greater than first) indicate that planes of mercury and sulphur alternate, but no definite decision as to the atomic positions can yet be made.

Molybdenite, MoS_2.[49]—The hexagonal cell of this structure contains two molecules, whilst $c = 12{\cdot}30$ Å.U. and $c/a = 3{\cdot}90$. The

[44] R. M. Bozorth, *J. Amer. Chem. Soc.*, 1923, **45**, 1621.

[45] Sir W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, 1923, [*A*], **104**, 437.

[46] L. W. McKeehan, *Physical Rev.*, 1923, **21**, 503.

[47] W. H. and W. L. Bragg, "*X*-Rays and Crystal Structure," old edition, p. 163.

[48] C. Mauguin, *Compt. rend.*, 1923, **176**, 1483.

[49] R. G. Dickinson and L. Pauling, *J. Amer. Chem. Soc.*, 1923, **45**, 1466.

structure is derivable from D_{6h}^4 as well as from D_{3h}^4, D_6^6, C_{6h}^2, and D_{3d}^2, which means that if the atoms can be considered as points or spheres, the symmetry is hexagonal holohedral. The co-ordinates of the molybdenum atoms are $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$, while those of the sulphur atoms are $(\frac{1}{3}, \frac{2}{3}, u)$, $(\frac{2}{3}, \frac{1}{3}, \bar{u})$, $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2} - \bar{u})$, and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + u)$, where $u = 0{\cdot}621 \pm 0{\cdot}004$. Each sulphur atom is equidistant from three molybdenum atoms, and each molybdenum is at the centre of a triangular prism of sulphur atoms. The molybdenum atoms are distant $2{\cdot}41 \pm 0{\cdot}06$ Å.U. from the nearest sulphur atoms, which is in good agreement with W. L. Bragg's "atomic radii." The perfect basal cleavage is apparently connected with the relatively great distance between the sulphur atoms.

Tin Tetraiodide.[50]—This crystal also belongs to the pyrites class and group, T_h^6. There are eight molecules in the unit cube, the side of which is 12·23 Å.U. Crystallographically, one of the iodine atoms is different from the other three, but this fact probably has no chemical significance, since all four are arranged tetrahedrally around the tin atoms. Apparently the distance from tin to iodine centres is 2·63 Å.U., but that between the nearest iodine atoms is 4·21 Å.U., which is the same as in the structure of cadmium iodide. The structure must be considered as molecular. This crystal has been examined by other workers also,[51] who, although uncertain of the space-group, draw similar conclusions regarding the atomic arrangement.

Potassium Hydrogen Fluoride.[52]—There are four molecules in a cell which is $5{\cdot}67 \times 5{\cdot}67 \times 6{\cdot}81$ Å.U. It is tetragonal and may be derived from D_{4h}^{18}, D_{2d}^{10}, or D_4^9. The structure may be regarded as an ammonium chloride arrangement of potassium atoms and fluorine dumb-bells, the two atoms in each dumb-bell lying in a plane perpendicular to the tetrad axis. There are two possible positions for the hydrogen atoms, one of which is in the middle of the fluorine dumb-bell, making a negative (HF_2) ion.

Sodium Chlorate.—The structure of this compound has given rise to a great deal of discussion, and much conflicting evidence and argument have been put forward. Apparently L. Végard [53] condemns the work of Kolkmeijer, Bijvoet, and Karssen,[54] but the three last-named are supported by R. G. Dickinson and E. A. Goodhue [55] and by W. Kiby,[56] whilst G. Wulff [57] has deduced yet

[50] R. G. Dickinson, *J. Amer. Chem. Soc.*, 1923, **45**, 958.
[51] H. Mark and K. Weissenberg, *Z. Physik*, 1923, **16**, 1.
[52] R. M. Bozorth, *J. Amer. Chem. Soc.*, 1923, **45**, 2128.
[53] *Z. Physik*, 1922, **12**, 289; 1923, **18**, 379.
[54] *K. Akad. Wetensch. Amsterdam*, 1921, **23**, 644.
[55] *J. Amer. Chem. Soc.*, 1921, **43**, 2045. [56] *Z. Physik*, 1923, **7**, 213.
[57] *Z. Krist.*, 1922, **57**, 190.

another structure. The crux of the matter is that we do not yet know enough about the scattering of *X*-rays to settle the question finally.[58] In all the work on sodium chlorate to date, there are involved certain unverifiable and perhaps unwarranted assumptions.

Silicon.[59]—All samples tested gave spectra conforming to the "diamond structure." The side of the elementary cube is 5·4204 ± 0·00016 Å.U. The different chemical activities of varieties of silica are due solely to differences in the ratio of surface to mass of the specimen.

Sulphides of Magnesium, Calcium, Strontium, and Barium, MgS,CaS,SrS,BaS.[60]—These all conform to the "rock-salt structure." The results are tabulated in the paper.

Calcite, $CaCO_3$.[61]—A critical discussion of the interpretation of the experimental results. The conclusions afford a new confirmation of W. L. Bragg's hypothesis.

Alkali Halides.[62]—By the powder method, precision measurements have been made of twenty alkali halides. The dimensions and densities together with probable error are given in the paper.

Natural and Synthetic Oxides of Uranium, Thorium, and Cerium.[63]—Pitchblende, bröggerite, cleveite, thorianite, and the oxides of uranium, thorium, and cerium have been examined by the powder and Laue methods. The dioxides are isomorphous and seem to conform to the "fluorspar structure." The cube sides are 5·47, 5·61, and 5·41 Å.U., respectively. The structure of uranosouranic oxide, U_3O_8, is irregular, and uranic oxide was obtained only in the amorphous form. The minerals thorianite (5·57 Å.U.), bröggerite (5·47½ Å.U.), and cleveite (5·47 Å.U.) correspond with isomorphous mixtures of the three oxides and lead peroxide. The ground lattice of all these minerals is uranous oxide, and it is supposed that the excess of oxygen corresponding with uranic oxide is present in solid solution. Bröggerite in which the uranium is partly transformed into lead retains the original lattice arrangement.

Silver Iodide, etc.[64]—By the powder method the author finds that silver chloride and bromide are of the rock-salt type with sides

[58] A. Karssen, *Rec. trav. chim.*, 1923, **42**, 904.
[59] H. Küstner and H. Remy, *Physikal. Z.*, 1923, **24**, 25.
[60] S. Holgersson, *Z. anorg. Chem.*, 1923, **126**, 179.
[61] C. Mauguin, *Compt. rend.*, 1923, **176**, 1331.
[62] W. P. Davey, *Physical Rev.*, 1923, [ii], **21**, 143.
[63] V. M. Goldschmidt and L. Thomassen, *Videnskafsselskapets Skrifter. Mat. Naturv. Klasse*, 1923, 5; from *Chem. Zentr.*, 1923, i, 1149.
[64] R. B. Wilsey, *Phil. Mag.*, 1923, [vi], **46**, 487.

5·540 and 5·768 Å.U., respectively. Silver iodide is cubic of the zinc sulphide type, side 6·493 Å.U., and hexagonal of the zinc oxide type with $a = 4·593$ Å.U. and $c/a = 1·633$. Metallic silver is face-centred cubic with side 4·078 Å.U. The question of the structure of silver iodide [64] is particularly interesting, and Wyckoff, in his "Survey of Existing Crystal Structure Data," has made some strong (but possibly unjust) comments on the subject. Wyckoff and others maintain that silver iodide is purely hexagonal at the ordinary temperature and cubic at temperatures above 146°, whilst Wilsey and Davey [65] claim that the lines of the cubic structure are observed in many samples at the ordinary temperature. In spite of Wyckoff's criticism, the conclusions of the two last-named workers are perhaps not unreasonable.

Lithium Halides.[66]—The author finds that anhydrous lithium chloride, bromide, and iodide are of the rock-salt type. The dimensions are given. The monohydrate of lithium chloride is of the cæsium chloride type.

Iron Carbide, Fe_3C.[67]—The author finds a rhombic lattice, $a = 4·481$ Å.U., $b = 5·034$ Å.U., $c = 6·708$ Å.U. The forms of cementite shown in the iron–carbon thermal diagram are not distinguishable by their lattice structure, and data taken above 210° show that the magnetic transformation is *not* associated with a change in the type of lattice.

Vitreous Carbon.[68]—This hard, lustrous, crystalline form of carbon is said to give a spectrum containing both graphite and diamond lines. It is dense (d_4 2·07) and very pure and can be prepared with a hardness greater than that of carborundum. Its electrical conductivity is low.

Lithium and Lithium Hydride.[69]—This investigation is particularly interesting as an attempt to locate the electrons in the two simplest crystal structures. Lithium is found to be centred-cubic with side 3·50 Å.U. A lattice of stationary electrons does not explain the results, and it is thought possible that the valency electron rotates round the nucleus or describes an orbit between the lithium-ions, in planes perpendicular to the trigonal axes, the radius in the latter case being larger than about one-fifth of the distance between the two ions (one-quantum orbits suffice). Lithium hydride is also cubic with four molecules per cell of side 4·10 Å.U. There appear to be two possible structures, both analogous to sodium

[65] W. P. Davey, *Physical Rev.*, 1922, **19**, 248.

[66] H. Ott, *Physikal. Z.*, 1923, **24**, 209.

[67] F. Wever, *Mitt. Kaiser Wilh.-Inst. Eisenforsch.*, 1922, **4**, 67; from *Chem. Zentr.*, 1923, iii, 187.

[68] K. A. Hofmann and C. Röchling, *Ber.*, 1923, **56**, [*B*], 2071.

[69] S. M. Bijvoet, *Rec. trav. chim.*, 1923, **42**, 859.

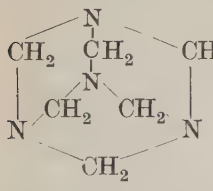
chloride : (1) in which atoms with radii of approximately the same order of magnitude as those calculated by Bohr for the free atoms are placed at the lattice points; (2) with positive lithium-ions and negative hydrogen-ions at the lattice points, the electrons rotating round the nucleus in paths the planes of which are perpendicular to the trigonal axes. Thus in lithium hydride there is a possibility of a heteropolar binding, whilst in lithium itself the binding is probably homopolar.

Hexagonal Zinc Sulphide and Nickel Arsenide.[70]—In these two hexagonal structures there are two molecules per cell. For ZnS, $a = 3{\cdot}80$ and $c = 6{\cdot}23$ Å.U., whilst for NiAs $a = 3{\cdot}57$ and $c = 5{\cdot}10$ Å.U. For both crystals two possible structures accord with the experimental results. These are given by the following co-ordinates. 1. Zn : (o, o, o), $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$; S : (o, o, p), $(\frac{2}{3}, \frac{1}{3}, p - \frac{1}{2})$. 2. Zn (or S) : (o, o, o), $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$; S (or Zn) : $(\frac{1}{3}, \frac{2}{3}, p)$, $(\frac{1}{3}, \frac{2}{3}, p - \frac{1}{2})$. For ZnS, the former arrangement is the more probable, where $p \sim \frac{1}{8}$, whilst for NiAs the latter is favoured, where $p \sim \frac{3}{4}$. If we accept these values of the parameters, the " atomic radii " are in good agreement with the values calculated from other crystals.

Calcium Thiosulphate Hexahydrate, $CaS_2O_3,6H_2O$.[71]—This crystal has hitherto been regarded as perhaps a unique example of the triclinic asymmetric class (1), but there are *two* molecules in the fundamental cell. It thus seems likely, from analogy with other complex structures, that the two molecules are inverse to each other, and the crystal is after all only one of the many examples of the triclinic pinakoidal class (2).

Structure of Organic Crystals.

Hexamethylenetetramine,[72] $C_6H_{12}N_4$.—The authors conclude that their data accord with a body-centred cube of edge 7·02 Å.U., in which there are two like molecules of $C_6H_{12}N_4$ of tetrahedral symmetry. Both the carbon atoms and the nitrogen atoms are equivalent among themselves, and this fact is brought out by the structural formula annexed. Two nitrogen atoms are about 1·44 Å.U. from each carbon atom, and at least approximately in the directions of two vertices of a tetrahedron.



Anthracene.[73]—The structure of this crystal is exactly analogous to that of naphthalene, monoclinic prismatic, with two molecules

[70] G. Aminoff, *Z. Krist.*, 1923, **58**, xi, 203.

[71] W. T. Astbury, *Nature*, 1923, **112**, 53.

[72] R. G. Dickinson and A. L. Raymond, *J. Amer. Chem. Soc.*, 1923, **45**, 22.

[73] W. H. Bragg, *Proc. Physical Soc.*, 1923, **35**, 167.

per cell. The major length of the molecule lies along the *c*-axis, and the difference in the lengths of this axis in the two cases is 2·5 Å.U., which corresponds exactly with the width of the benzene ring. The calculated density, 1·255, also agrees with an experimental determination. The molecular symmetry of naphthalene and of anthracene in the crystalline state is centro-symmetry only.

Anhydrous Racemic Acid.[74]—The crystallographic cell is not the true fundamental cell, since it is associated with a half-molecule of *d*- and a half-molecule of *l*-tartaric acid, that is, alternate corners of the (001) face are occupied by active molecules of the same sort. There is no evidence from the *X*-ray examination that racemic acid exists as an independent inactive doublet of molecular weight 300. The chemical molecule in racemic acid is substantially of the same shape and dimensions as the molecule in active tartaric acid, but a small contraction in the length of the molecule and the absence of a certain cleavage appear to be associated with small changes in physical properties which accompany the formation of racemic acid from its active components. The disappearance of the distortion of the hydroxyl groups of tartaric acid favours the hypothesis of the anomalous optical properties of the active acid. An explanation is given of the multiple twinning and irregular growth of anhydrous racemic acid.

Urea.[75]—The authors have shown that the structure of this interesting substance can be determined independently of crystallographic and chemical characteristics, since there is only one space-group and one atomic arrangement which are compatible with the *X*-ray results. It is tetragonal scalenohedral, space-group D_{2d}^3, with $a = 5{\cdot}63$ Å.U. and $c = 4{\cdot}70$ Å.U. There are two molecules per cell, which means that each molecule possesses the symmetry C_{2v}, that is, two mutually perpendicular planes intersecting in a diad axis. The distance between the centres of two adjacent molecules lies between 3·98 and 4·62 Å.U.

Pentaerythritol.[76]—The structure of this compound, more interesting still than that of urea, has been elucidated by the same authors. It is ditetragonal pyramidal, with $a = 6{\cdot}16$ Å.U. and $c = 8{\cdot}76$ Å.U. It is body-centred, contains two molecules of $C_5H_{12}O_4$, and belongs to the space-group C_{4v}^9. But the most striking conclusion is that the symmetry of the molecule is C_{4v}, that is, four planes of symmetry inclined at 45° to each other and intersecting in a tetrad axis. This symmetry must be shared by the central carbon atom, about which the four substitution groups ($\cdot CH_2 \cdot OH$) are structurally equivalent

[74] W. T. Astbury, *Proc. Roy. Soc.*, 1923, [*A*], **104**, 219.
[75] H. Mark and K. Weissenberg, *Z. Physik*, 1923, **16**, 1.
[76] *Idem, ibid.*, 1923, **17**, 301.

and lie in the hemimorphic planes of symmetry. This important result means that the valency bonds of the central carbon atom are *not* arranged tetrahedrally, but point towards the four corners of a square.

Basic Glucinum Acetate and Propionate.[77]—The structure of the basic acetate, $Gl_4O(CO_2{\cdot}CH_3)_6$, has been already mentioned. It is highly interesting and important chemically, but the results of the crystal analysis are no less fascinating. The crystal is built, like arsenious oxide, on the "diamond structure," space-group O_h^7, that is, in each unit cube there are eight molecules each possessing the symmetry of a regular tetrahedron. The side of the unit cube is 15·72 Å.U. The outstanding feature of these observations is the conclusion with regard to the molecular symmetry. Basic glucinum acetate is extremely stable and is associated with remarkable chemical and physical properties. It is a co-ordination compound built round a unique central oxygen atom. The four glucinum atoms are grouped tetrahedrally round this central oxygen atom, whilst the six acetate groups span the six edges of the tetrahedron. Such an arrangement is capable of simple interpretation in terms of the electronic theory of valency, but it must be remembered that the molecule possesses the 24-fold symmetry of a *regular* tetrahedron, that is, the acetate groups which span the edges must each be symmetrical about a plane. Consequently, the ordinary structural formula does not apply to them. The original difference between hydroxyl and carboxyl oxygens has been smoothed out by the presence of a plane of symmetry. The co-ordinated acetate group must be looked upon as $CH_3—C\lessdot^{O\cdots}_{O\cdots}$. Some as yet unpublished observations [78] on the symmetry of the acetylacetones lead to similar conclusions. Basic glucinum propionate has been shown to belong to the monoclinic system, with two molecules per cell (which is probably monoclinic prismatic). The molecule is either centre-symmetrical or nearly so. Beyond this, nothing can be concluded with certainty.

Starch.[79]—The author claims that starch is built on a tetragonal lattice, $5{\cdot}94^2 \times 5{\cdot}05$ Å.U., with one group, $C_6H_{10}O_5$, in such a cell. This result is approached with caution, since the number and quality of the spectral lines obtained from starch are both somewhat inadequate.

Various Compounds.[80]—The authors have made by the *X*-ray method measurements of the cells of various organic substances.

[77] Sir W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, 1923, [*A*], **104**, 437.
[78] W. T. Astbury. [79] O. L. Sponsler, *J. Gen. Physiol.*, 1923, **5**, 757.
[80] K. Becker and H. Rose, *Z. Physik*, 1923, **14**, 369.

Abnormal Reflection of X-Rays.[81] [82]

A series of papers, dating from May, 1922, have appeared on the subject of the reflection by a crystal of *X*-rays characteristic of the elements in it. The authors, using an ionisation spectrometer and the "white" radiation from a tungsten target, claim that in addition to the ordinary reflections which are observed on Laue photographs, they have observed certain abnormal reflections of rays characteristic of the elements constituting the crystal examined. For instance, when examining potassium iodide crystals, they claim to have observed the *iodine* lines besides the usual tungsten lines. The values of the wave-lengths producing these abnormal reflections were obtained by determining the critical voltages below which the reflections did not occur and combining these results with the quantum relation. Some of these reflections appear to obey Bragg's law, whilst others do not, but by the aid of those that do obey the law the authors state that they have found the spacings of the atoms giving rise to the characteristic rays. Thus they have put forward structures for the polyhalides KI_3, CsI_3, $CsIBr_2$, and $CsICl_2$. For CsI_3, it is stated that the spacing of the iodine atoms is one-quarter that of the cæsium atoms, and that therefore the crystal unit is a rectangular parallelepiped with cæsium atoms at the corners and iodine atoms at the centre and equidistant along the body-diagonal. The results for the other polyhalides are similar, the heaviest halogen being at the centre of the body-diagonal. The halogen atoms constitute a singly-acting group just as they do in the formation of complex ions in solution. The stability of the polyhalides is apparently directly proportional to the atomic volumes of the metals.

No one else seems to have been able to detect the effect described by Clark and Duane, and it must be confessed that their interpretation is not as yet generally accepted. The effect should be easily noticeable on Laue photographs, but Wyckoff [83] has failed to detect any trace of it. If it is a true effect, it is highly important and marks a new advance in the development of crystal analysis. Nothing is more desirable than to be able to detect the periodicity of individual atoms. When we can do that, the science will be almost complete.

Miscellaneous Papers.

Cohesion and Molecular Forces.—At the recent meeting of the British Association at Liverpool a joint discussion on cohesion and

[81] G. L. Clark and W. Duane, *Proc. Nat. Acad. Sci.*, 1922, **8**, 90; 1923, **9**, 117, 131.

[82] *Idem, J. Optical Soc. Amer.*, 1923, **7**, 455.

[83] *Amer. J. Sci.*, 1923, [v], **6**, 277.

molecular forces was held. The discussion was opened by Sir Wm. Bragg, who examined the question from the point of view of the results of *X*-ray analysis. The point he emphasised was that it appears to be necessary to say that the very strong forces between atom and atom, molecule and molecule, are limited in their effective range of action to distances much smaller than we have hitherto supposed. It seems nearer the truth to think that the exact adjustment in crystal structure is brought about, not by forces between points representing the molecules, but by the close association of certain points of one molecule with certain points of the next, that is to say, in considering the binding of the individual molecules of a solid, the analogy of the electrostatic attraction of two charged spheres is imperfect. Rather should it be replaced by that of two members of a girder structure adjusted until the rivets can be dropped into the holes provided for them. A significant example of this process is afforded by the long-chain compounds described above. In them, the forces associated with the ends of the molecule appear to be without effect on the atomic arrangement of the middle of the molecule. Dr. Rosenhain, who followed, discussed the problem of alloys and pure metals from the point of view of the considerations already set out above, whilst Dr. A. A. Griffith asked that physicists should study thoroughly the collapse of space-lattices under shearing stress. Prof. Lindemann declared that the assumptions of previous speakers with regard to bonds were premature, and Sir Oliver Lodge added the final touch by saying that we do not yet know why, when we raise one end of a stick from a table, the rest of the stick also comes up.

Structure of Benzene, etc.[84]—A theoretical paper. In diamond, each carbon is surrounded tetrahedrally by four electron-pairs, but in graphite the alternative arrangement must hold, that is, there must be an electron pair between the nearest atoms in adjacent layers and a *sextet* of electrons around the centre of each hexagon. Such an arrangement accounts for the tightening of the hexagons and their wider distance apart and also for physical and crystallographic properties. Huggins rejects Hull's structure for graphite, but suggests an alternative hexagonal structure. But this point is immaterial; the chief point is the existence of the hexagon first suggested by Körner in 1874. Applying the valency theory to this, we get a sextet in the centre, an electron-pair joining carbon to hydrogen, and an electron pair at each of the hexagon corners. If units of this type are close-packed side by side, they form a layer in which the molecular boundaries are no longer distinguishable.

[84] M. L. Huggins, *J. Amer. Chem. Soc.*, 1923, **45**, 264; *Amer. Ass. Adv. Sci.*, Aug. 5th, 1921.

Removing the hydrogen atoms and placing layer upon layer in such a way as to produce C—C bonds where C—H bonds had been gives one or other of two possible graphite structures : (*a*) modified Debye-Scherrer structure, (*b*) Huggin's hexagonal structure. Now assume that crystals of benzene, etc., are formed of close-packed layers of hexagons. Then, for example for quinol, $\rho = 1{\cdot}33$, $a/c = 1/0{\cdot}6680$ and mol. vol. (V) = 136·54. If the distance between the layers is c and there are n molecules per cell, volume of unit cell = $nc \times 15{\cdot}84$ (area of ring) = nV. Therefore $c = 8{\cdot}61$, $a = 12{\cdot}9 = 6 \times 2{\cdot}15$. By this method and extensions of it, Huggins has deduced the ring dimensions from *eleven* compounds, and they all agree closely with the graphite dimensions. Moreover, he explicitly states the limitations of the method. In certain cases, the molecular, atomic, and electronic arrangements are determined.

Electronic Structure of the Spinels.[85]—The interatomic distances are calculated and the conclusion is drawn that the empirical formula $R''R'''_2O_4$ is the only one which correctly represents the structure in the crystalline state.

Crystal Cleavage and Structure.[86]—The following rules governing crystal cleavage are presented : (1) Cleavage tends to occur so as to leave the two new crystal surfaces electrically neutral. (2) Weaker bonds will be broken in preference to the stronger bonds. (3) If all bonds are equally strong, cleavage will occur between the planes connected by the fewest bonds per unit area. These rules are used to explain satisfactorily the observed cleavage in diamond, sphalerite (ZnS), wurtzite (ZnS), sodium chloride, iron pyrites, calcite, aragonite, graphite, antimony, and bismuth.

Isomorphism in the Organo-metallic Series.[87]—A study of the temperatures of fusion and solidification of binary mixtures of oxides and sulphides of triphenyl-phosphine, -arsine, and- stibine. The results indicate that if in a pair of organo-metallic compounds the asymmetry of the central atoms is increased by the addition of oxygen in one and of sulphur in the other, the tendency to isodimorphism is increased. If, on the other hand, the central atoms are saturated by the same element, oxygen or sulphur, the tendency to isomorphism is increased.

Structure of Halides from Compressibility.[88]—A theoretical paper. Calculations, based on Sir J. J. Thomson's hypothesis, are made of the compressibilities of various cubic halogen salts; values are obtained which are in good agreement with the experimental values

[85] M. L. Huggins, *Physical Rev.*, 1923, **21**, 509.
[86] *Idem*, *Amer. J. Sci.*, 1923, **5**, 303.
[87] P. Pascal, *Bull. Soc. chim.*, 1923, [iv], **33**, 170.
[88] Ida Woodward, *Phil. Mag.*, 1923, [vi], **45**, 882.

of Richards and Jones. In addition, the specific photoelectric effect and the specific inductive capacity for the sodium and potassium salts are calculated with the aid of W. L. Bragg's atomic diameters.

Refraction and Absorption of Light by Zinc Blende.[89]—These quantities were measured for temperatures ranging from $-80°$ to 700° and for wave-lengths between 400 and 800μ. The results indicate that in the visible spectrum the dispersion is normal and attributable principally to an oscillator with a frequency in the ultra-violet.

Optical Activity of Sodium Chlorate and Sodium Bromate.[90]—A theoretical paper. The author uses Born's theory of crystal lattices to deduce expressions for the optical rotatory powers. Observed and calculated values for sodium bromate agree well for wave-lengths between 4 and 8×10^{-5} cm., but for sodium chlorate the calculated values are approximately only one-half of the experimental values. This result indicates the necessity for considerable alteration of the lattice model used in developing the theory, possibly effected by a displacement of the centre of mass of the electrons, a procedure possible only with Végard's model.

Rotatory Dispersion.[91]—In this paper it is shown that optical activity depends on the presence of an axially symmetrical system of at least four coupled electrons, which may be carried either by a single atom or by several atoms of the molecule. An active molecule may contain more than one of such electron systems, and consequently the rotatory dispersion may exhibit an abnormal character. Besides the rotatory dispersion, the Cotton effect, absorption, and circular dichroism are discussed. The rotatory dispersion of a large number of heavy-metal complex derivatives and organic substances has been investigated and the results have been considered from the point of view of spectroscopic, photochemical, and stereochemical data.

The Structure of Thin Films.[92]—Although not belonging to the subject of crystallography proper, these papers should be read in connexion with the *X*-ray investigation of long-chain compounds described above.

Dimensions of Molecules, Atoms, and Ions.[93]—A critical *résumé* of the literature on this subject and a discussion of the relative accuracy of the different methods of determining molecular dimensions—viscosity, critical data, *X*-ray analysis, measurement in liquids, diamagnetism, optical measurements. Much smaller dimensions

[89] Maria Mell, *Z. Physik*, 1923, **16**, 244.
[90] C. Hermann, *ibid.*, p. 103.
[91] I. Lifschitz, *Z. physikal. Chem.*, 1923, **105**, 27.
[92] N. K. Adam, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 676, 687.
[93] K. F. Herzfeld, *Jahrb. Radioaktiv. Electronik*, 1923, **19**, 259.

are obtained for molecular dimensions in the gaseous than in the crystalline state, and this is ascribed to the occurrence of phase relationships between the electron orbits in the latter case which considerably increase the repulsive forces.

Paramagnetism at Low Temperatures.[94]—A complete investigation is given of the susceptibilities, down to the lowest temperature obtainable with liquid hydrogen, of the anhydrous sulphates, the heptahydrated sulphates, and the ammonium double sulphates of cobalt, nickel, and ferrous iron, all in the powder form; and of two complete crystals, cobalt ammonium sulphate and nickel sulphate heptahydrate. The last-named are the only data yet available of the principal susceptibilities of crystals at the lowest temperatures. In all the cases examined, the susceptibilities follow the Weiss Law, $\chi(T + \Delta) = C$ at higher temperatures, but various deviations are found at the lowest temperatures. For the complete crystals, the Curie constant is the same for each of the three principal susceptibilities, and these increase more rapidly with fall of temperature than is given by the Weiss Law, which is obeyed at higher temperatures. There does not seem to be an intimate connexion between the " magnetic dilution " of a substance and the Δ of the Weiss Law, but the connexion between Δ and the spacings of the paramagnetic atoms has been used to construct a hypothetical space-lattice for the nickel atoms of the sulphate heptahydrate. Apparently, this suggested lattice is in agreement with an X-ray powder photograph, and it would be interesting to have the structure worked out thoroughly. The above low-temperature investigations are extended in a subsequent paper[95] to cobalt potassium sulphate, cobalt rubidium sulphate, and manganese ammonium sulphate.

Universal Interferometer and Wave-length Torsometer.[96]—For details of these ingenious instruments reference should be made to the original papers.

Thermal Conductivity of Bismuth Crystals.[97]—This quantity has been determined for directions parallel and perpendicular to the trigonal axis. The values at 18° in C.G.S. units are: (*a*) Parallel to trigonal axis, 0·0159, (*b*) perpendicular to trigonal axis, 0·0221. Ratio = 1·39. A new " plate " apparatus has been developed which makes it possible to measure thermal conductivities as high as 0·02 C.G.S. unit with the accuracy of about 1 per cent., using specimens 2 cm. by 1 cm. and about 1 or 2 mm. in thickness.

Rotatory Polarisation in an Orthorhombic Crystal exhibiting Crossed

[94] L. C. Jackson, *Phil. Trans.*, 1923, [*A*], **224**, 1.
[95] L. C. Jackson and H. K. Onnes, *Proc. Roy. Soc.*, 1923, [*A*], **104**, 671.
[96] A. E. H. Tutton, *ibid.*, pp. 47, 62.
[97] G. W. C. Kaye and J. K. Roberts, *ibid.*, p. 98.

Axial Dispersion.[98]—Crystals of triphenylbismuthine dichloride (orthorhombic holoaxial, $a : b : c = 0{\cdot}774 : 1 : 0{\cdot}409$) are uniaxial for green light of wave-length 510 $\mu\mu$ at 17°. They exhibit the phenomenon of crossed axial dispersion, and a section perpendicular to the acute bisectrix does *not* extinguish between crossed nicols, but transmits light of a bright green colour. Similar phenomena are shown by potassium sodium tartrate. A salt of one part of sodium potassium tartrate and two parts of sodium ammonium tartrate is uniaxial in the green, whilst a salt of equal proportions is uniaxial in the blue. These highly interesting observations of optical activity in biaxial crystals lead us finally to one of the most important optical researches in recent times :—

Rotatory Polarisation in Crystals, especially Biaxial Crystals.[99]—L. Longchambon has shown that in reality the number of active crystals is considerable. The majority of crystals in which the dissymmetry is structural and all those in which it is molecular have been found to be optically active. The author has devised a special arrangement whereby an extremely parallel beam of monochromatic light can be produced. He has shown that very little deviation from parallelism is sufficient to mask the rotatory polarisation of crystals, but with the new system the most feeble effects have been observed and measured. The crystals examined include lead, barium, and strontium formates, nickel and zinc heptahydrated sulphates, magnesium chromate, ammonium oxalate, iodic acid, hydrazine sulphate, sodium arsenate, and lithium sulphate. The only exceptions are the cubic nitrates of lead, barium, and strontium, but since in Wyckoff's "Survey" these substances are described as belonging to the pyrites class, this result is not to be wondered at. On seven chosen examples, it has also been shown that the rotatory dispersion has exactly the same value whether the substance is liquid, dissolved, or crystalline. From these results, Longchambon proposes two generalisations, (1) that the rotatory dispersion is independent of the direction of observation; (2) that the rotatory power due to structure, if it exists in these crystals, has the same rotatory dispersion as the chemical molecules which constitute the crystal.

New Books, Etc.

An English edition of Rinne's "Das feinbauliche Wesen der Materie nach dem Vorbilde der Kristalle" (translated by W. S. Stiles) has been published by Messrs. Methuen.

In June there appeared "Kristalle und Röntgenstrahlen" from the pen of Dr. P. P. Ewald (Berlin : Julius Springer, pp. viii + 327). Ewald has always been one of the foremost in the ranks of crystal-

[98] G. Greenwood, *Min. Mag.*, 1923, **20**, 123.
[99] *J. Physique*, 1922, [iii], **6**, 156S.

analysts, and a first-hand discussion of the subject from such a master is extremely welcome. The book deals with both crystal-structure and *X*-rays, and the science is developed step by step in such a way as to give a thorough and comprehensive account of the progress from the discovery of Laue to the present time. The various methods of attacking the problem are carefully described and many interesting chemical and physical points considered from the new point of view. At the end are a number of Notes on more difficult and specialised branches, and a very complete list of papers on crystals analysed and related physical topics.

One of the founders of the structure-theory, Prof. Schoenflies, has rewritten his epoch-making work "Krystallsysteme und Krystallstruktur." The new edition ("Theorie der Kristallstruktur. Ein Lehrbuch," Berlin (Borntraeger), 1923, xii + 555 pp., 257 figs., 18*s*.), is largely unaltered, but it is adapted for the benefit of modern crystal-analysts, and the subject is viewed in the light of recent researches. But the subject must always remain to a large extent mathematical, and, on account of this, this new edition from the pen of one of the pioneers of the science is specially recommended to the mathematical crystallographer. For the object for which it is intended it is invaluable.

"A Survey of Existing Crystal Structure Data," by R. W. G. Wyckoff,[1] is a very useful addition to the literature of the subject.

A new edition of "X-Rays and Crystal-Structure" by W. H. and W. L. Bragg is now in the press.

Volume III of "Minéralogie de Madagascar" (A. Lacroix, Paris, Soc. d'éditions géogr. 1923, viii + 450 pp. 4°, 8 pls., geol. map, 28 text figs.) has appeared, and this handsome topographical mineralogy is now complete.

A very cheap (1*s*.) second edition of the "Guide to the collection of gemstones in the Museum of Practical Geology" (W. F. P. McLintock, London, 1923, iv + 80 pp., 24 figs.) has been published on much the same lines as the first edition. A fifth edition of "Grundriss der Kristallographie" [G. Linck, Jena (G. Fischer), 1923, x + 293 pp., 3 col. pls., 521 text figs.], has also appeared.

This Report cannot be better concluded than by reference to the latest edition of the *Zeitschrift für Kristallographie*,[2] prepared specially in honour of the eightieth birthday of the foremost crystallographer of our time, Professor P. H. v. Groth. Contributions from the leading crystallographers and mineralogists of the world have been laid at his feet, and the volume is at once a valuable addition to scientific literature and a fitting tribute to a brilliant genius and a notable personality.

W. T. Astbury.
W. H. Bragg.

[1] *J. Frankl. Inst.*, 1923, **195**, 183, 349, 531. [2] *Z. Krist.*, 23 June, 1923.

MINERALOGICAL CHEMISTRY.

Distribution of Chemical Elements in the Earth's Crust.

A TABULATED compilation of 8,611 chemical analyses of igneous rocks published between the years 1884 and 1913 has been given by H. S. Washington.[1] From a selection of 5,159 of the more trustworthy of these analyses, F. W. Clarke and H. S. Washington [2] have calculated the average composition of the rocks of various countries and regions, but these being arbitrary political divisions only small accidental variations are shown. Their new average for all igneous rocks is quoted in part under I. Including also sedimentary rocks (shale estimated at 4·00 per cent., sandstone 0·75 per cent., and limestone 0·25 per cent.) in a lithosphere ten miles in thickness, and also the hydrosphere and atmosphere, their estimate of the average chemical composition of the accessible portions of the earth is given under II :

	O.	Si.	Al.	Fe.	Ca.	Na.	K.	Mg.
I.	46·41	27·58	8·08	5·08	3·61	2·83	2·58	2·09
II.	49·19	25·71	7·50	4·68	3·37	2·61	2·38	1·94

	H.	Ti.	Cl.	P.	C.	Mn.
I.	0·129	0·720	0·096	0·157	0·051	0·124
II.	0·87	0·648	0·228	0·142	0·139	0·108

The fourteen elements listed under II total 99·517 per cent., and the eighteen others separately estimated range from sulphur 0·093 per cent. to boron 0·001 per cent.

Speculations as to the composition of the interior of the earth can only be based on a comparison of the observed densities of superficial rocks (mean 2·77) and that of the earth as a whole (viz., 5·55). H. S. Washington,[3] in a paper on "The Chemistry of the Earth's Crust," distinguishes "petrogenic" elements of low atomic weight characteristic of igneous rocks, and "metallogenic" elements of higher atomic weight. He assumes that the core of the earth is made up of heavier metallogenic elements (platinum, etc.) either free or as arsenides, tellurides, etc.; and that between the core and the silicate crust there is a zone of nickel-iron. V. M.

[1] *Prof. Paper U.S. Geol. Survey*, 1917, No. 99, 1201 pp.
[2] *Proc. Nat. Acad. Sci.*, 1922, **8**, 108.
[3] *J. Franklin Inst.*, 1920, **190**, 757.

Goldschmidt [4] supposes that under the influence of gravity the interior of the earth has separated into four well-marked zones: (1) a core of heavy metals, chiefly nickel-iron, and represented by meteoric irons; (2) a zone of metallic oxides and sulphides, represented in meteorites by troilite and chromite nodules; (3) a zone of dense silicates, called the eclogite shell; and (4) a thin outer shell of lighter silicates. The chemical elements proper to these zones and to the atmosphere he places in four main groups: (1) "siderophil" elements (Fe, Ni, Co, P, C, Mo, Pt, Ir, etc.); (2) "chalcophil" elements (S, Se, Te, Fe, Cu, Zn, Pb, As, Sb, Bi, Ag, Au, Hg, Pd, etc.); (3) "lithophil" elements of silicate fusions (O, Si, Ti, F, Cl, Al, Ce, Na, K, Gl, Mg, Ca, V, etc.); (4) "atmophil" elements (H, N, He, A, etc.). Seismologists have deduced the presence in the earth of three zones with the thicknesses and densities stated below, the middle layer with a density of 5·6 having a calculated thickness of 1,400 kilometres. These three zones are compared by G. Tammann [5] with the slag, sulphide, and metal layers in a crucible. Arranging the metals in relative order from electro-positive to electro-negative, he points out that those more positive than iron are the ones that are abundant in the silicate crust, whilst those more negative than iron include the precious metals and would be expected to be more abundant in the metal zone. The composition deduced for the three zones is as follows:

	Thickness in km.	Density.	Composition.
Silicate crust ...	0—1500	2·9	$1(Al_2O_3,Fe_2O_3,FeO,CaO,MgO,K_2O,Na_2O),1\frac{1}{2}SiO_2$
Sulphide layer ...	1500—2900	5·6	FeS; Fe_3P; FeO; Fe; SiO_2
Metallic core ...	2900—6370	9·6	Fe 88%; Ni 8%; (Fe, S, P) 3%; precious metals 1%

P. N. Chirvinsky [6] compares the hypothetical zones of a pyrogenic globe with the progressive series: igneous rocks, meteoric stones, pallasites, and meteoric irons. Treating these as pseudo-elements, he calculates from the means of numerous analyses their equivalent atomic weights, which divided by densities gives a constant. This is held to be a consequence of Avogadro's law when the different zones were in a gaseous state. He also adds "terrium" or primordial matter, representing the average for the whole earth. From a

[4] *Videnskaps. Skrifter, Kristiania*, 1922, No. 11, and 1923, No. 3; *Z. Elektrochem.*, 1922, **28**, 411.

[5] *Z. anorg. Chem.*, 1923, **131**, 96.

[6] *Izv. Don. Polytech. Inst., Novocherkassk*, 1915, **4**, 76; 1918, **6**, suppl.; 1919, **7**, 94; 1923, **8**, 68; *Bull. Acad. Sci. Petrograd*, 1917, **11**, 387; [*Min. Mag.* (*Abstr.*), 1923, **2**, 82—85, 157.]

comparative study of meteorites and igneous rocks he attempts to evolve a system of "cosmochemistry."

Pseudo-element.	Equivalent composition.	At. wt.	d.	At. wt. / d.
"Crustaterrium"	$RSiO_3$	20·56	2·806	7·327
"Chondrium"	$R_2SiO_4 + RSiO_3$	24·36	3·4	7·165
"Pallasium"	$R_2SiO_4 + 3R$	30·90	4·66	6·63
"Siderium"	R	55·72	7·693	7·243
"Terrium"	—	39·98	5·5	7·269

Another suggestion touching a possible change in chemical elements during geological time has been made by J. Joly [7] in connexion with his examination of the pleochroic haloes surrounding minute crystals of radioactive minerals enclosed in biotite. Measurements of the thorium-haloes correspond exactly with the theoretical dimensions, but in the uranium-haloes, although the outer features are in good agreement with the calculated values, both the second and first rings appear to be displaced outwards. The explanation suggested is that the range of the α-rays, which attend the first stages of the radioactive change of uranium, has diminished in geological time—an effect which might be due to the existence of uranium atoms derived from some antecedent element possessing different radioactive properties from the uranium of the present time. A new type of halo, seen as minute, colourless or bleached spherical spots in a biotite from Sweden, is believed to be due to nuclei of a radioactive substance containing an element emitting α-rays of very low velocity. This element, although possibly identical with yttrium, is perhaps new, and it is provisionally named "hibernium." [8]

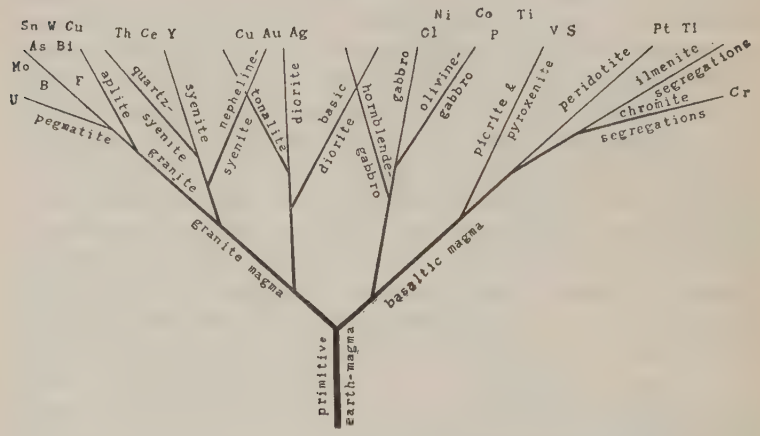
Returning to more practical considerations concerning the distribution of chemical elements in the accessible portions of the earth's crust, where during geological time there has been a constant re-sorting of material, it has long been recognised that certain elements are associated with certain types of rock, for example, tin with granite, platinum with olivine-rocks, and that certain groups of elements usually go together. This is enlarged on in the papers of H. S. Washington and V. M. Goldschmidt quoted above, and an instructive diagram (Fig. 1) has been given by R. H. Rastall.[9]

Although the distribution of the elements appears to be quite capricious, yet there is promise that the study of the differentiation of rock-magmas and the segregation of ore-deposits will in time lead

[7] *Phil. Trans.*, 1917, [*A*], **217**, 51.
[8] J. Joly, *Proc. Roy. Soc.*, 1923, [*A*], **102**, 682.
[9] "The Geology of the Metalliferous Deposits," Cambridge, 1923.

to some guiding principles. P. Niggli's recent text-books [10] contain much suggestive material on the paragenesis of minerals, and W. Lindgren [11] writes on the "Concentration and Circulation of the Elements from the Standpoint of Economic Geology." J. W. Gregory,[12] in his lecture before this Society on "Ore Deposits in relation to Geographical Distribution," suggested the occurrence of local uprisings of the metal-rich barysphere along continental margins at different periods of mountain-building. He pointed out that the more volatile mercury [13] ores are limited to regions of the later Alpine mountain-building, that tin ores are exposed in the earlier

FIG. 1.



Genealogical tree showing connexion of metals with igneous rocks.
(After R. H. Rastall, 1923.)

and more denuded Hercynian system of mountain-folding, whilst the most productive gold-quartz lodes are of still deeper-seated origin and only exposed in the oldest rocks.

Dealing with the geographical distribution of minerals as commercial sources of supply of crude material, a valuable series of pamphlets is now being issued by the Imperial Mineral Resources Bureau,[14] in which are given particulars of the mode and place of

[10] "Lehrbuch der Mineralogie," Berlin, 1920; "Gesteins- und Mineralprovinzen," Berlin, 1923.

[11] *Econ. Geol.*, 1923, **18**, 419.

[12] *T.*, 1922, **121**, 750.

[13] It is a noteworthy fact that no mercury-bearing mineral has ever been found in the British Isles.

[14] "The Mineral Industry of the British Empire and Foreign Countries, War period 1913—19," and a second series of "Statistics, 1919—21," London, 1921—24.

occurrence and statistics of production, together with detailed bibliographies. Each part (some sixty having already been issued) deals with a particular metal or mineral or group of minerals of economic importance; for example, Antimony, Cobalt, Tungsten, Vanadium, Asbestos, Graphite, Monazite, etc. Much information respecting the distribution of minerals is buried in the pages of books and papers on topographical mineralogy, and often this is of more than mere local interest. A notable work of this type is A. Lacroix's "Minéralogie de Madagascar" (Paris, 1922—23) recently issued as three large quarto volumes. Detailed descriptions of the characters and modes of occurrence, together with many chemical analyses, are given of some 200 mineral-species that have been recorded from Madagascar. The chapters on petrology include more than 450 new chemical analyses of rocks; and special attention is directed to the pegmatites, which carry a variety of rare-earth and radioactive minerals, these being compared in detail with similar occurrences in other parts of the world. Mention may also be made of P. P. Pilipenko's work on the minerals and ore-deposits of the Altai Mountains.[15] Descriptions and analyses are given of numerous metalliferous and other minerals. Of 713 occurrences, details are known as to the country-rock for 582; of these 4·6 per cent. are in granite, 2·6 per cent. in greenstone, 18·4 per cent. in quartz-porphyry, and 74·4 per cent. in sedimentary (mostly Devonian) rocks. They are, however, always in the neighbourhood of granite masses. Three main zones in depth are distinguished on chemical grounds: (1) The ochre or oxy-zone, this being further sub-divided downwards into (*a*) hydrate zone, (*b*) carbonate zone, and (*c*) sulphate zone. (2) The sooty-ore or sulphoxy-zone, with the secondary monosulphides Cu_2S and Ag_2S. (3) The primary sulphide or sulpho-zone. In the order of decreasing solubility the sulphides are: pyrites—sphalerite—chalcocite—galena—argentite; and of these the more difficultly soluble sulphides of silver, lead, bismuth, and copper were accumulated in the upper portion of the sulpho-zone. In the sulphoxy- and oxy-zones, the minerals are sharply differentiated according to their degree of solubility. Thermochemically, almost all the minerals are exothermic; minerals with low heat of formation are characteristic of the sulpho-zone, whilst those with greater heat of formation belong mainly to the upper zones.

Constitution of Silicates.

The key to the constitution of mineral silicates still remains to be discovered, and until then no satisfactory classification of this

[15] "Mineralogy of the Western Altai" (Russ.) *Izv. Imp. Tomsk. Univ.*, 1915, **63**, 763 pp. [*Min. Mag.* (*Abstr.*), 1923, **2**, 109.]

complex group of minerals can be expected. A useful outline has been given in T. M. Lowry's "Inorganic Chemistry" (London, 1922). J. Jakob [16] has devised a long series of constitutional formulæ based on Werner's co-ordination theory. For example, he writes the formulæ of enstatite, regarded as a trisilico-hexaoxy-silicate, and orthoclase, as a hexasilico-tetraoxy-silicato-salt, respectively, as follows :

$$\left[Si\left(\begin{matrix}O\\O\end{matrix}Si\begin{matrix}O\\O\end{matrix}\right)_3\right]Mg_4(Fe) \quad \text{and} \quad [Al(SiO_4SiO_2SiO_2)_3]^{Al_2}_{K_3}$$

This is rejected by B. Gossner,[17] who works out on paper an equally fantastic scheme. Here the composition is expressed by the combination, analogous to double salts, of certain simple molecules, for example :

Anorthite	$SiO_3Ca,[SiO_2,Al_2O_3]$.
Grossularite	$[SiO_3Ca,[SiO_2,Al_2O_3]],SiO_4Ca_2$.
Natrolite	$[SiO_3Na_2,[SiO_2,Al_2O_3]],SiO_2,2H_2O$.
or	$SiO_3Na_2,[2SiO_2,AlO_2H,AlO_3H_3]$.

Important experimental work bearing on this problem has been done for several years past in the Geophysical Laboratory of the Carnegie Institution at Washington. Although, primarily, this work was undertaken from rather another point of view, namely, to determine the conditions of formation of the various rock-forming minerals in igneous rocks. The composition of the products obtained in the synthetic experiments is expressed by the isomorphous mixing of end-members, these end-members being definite compounds and their composition expressed by more or less complex groups of oxides. Any deviation from such a composition has usually been explained by the adventitious solid solution or adsorption to a limited extent of some other oxides or groups of oxides in the main mixture. As an example of this work may be cited the system CaO–MgO–Al_2O_3–SiO_2, which was commenced in 1906 with the investigation of the calcium and magnesium metasilicates, wollastonite and pseudo-wollastonite, enstatite and clinoenstatite. The several binary and ternary systems of this group were separately examined, and they have been already referred to in these Reports with the exception of the last published,[18] namely, the system CaO–MgO–SiO_2. The thermal relations of numerous fusions of known composition were investig-

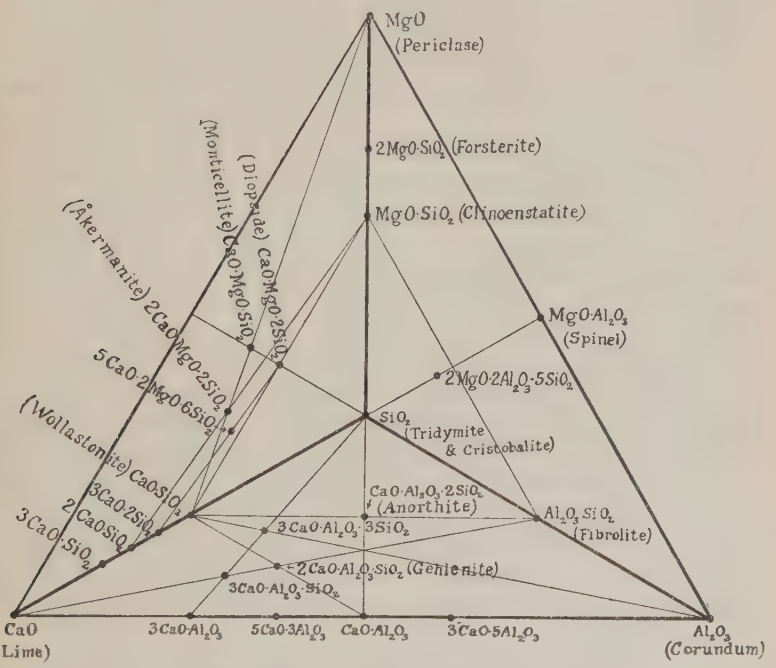
[16] *Helv. Chim. Acta*, 1920, **3**, 669; *A.*, 1920, ii, 754; *Z. Krist.*, 1921, **56**, 295.

[17] *Centr. Min.*, 1921, 513; 1922, 129, 193, 600, 625; *A.*, 1921, ii, 649.

[18] J. B. Ferguson and H. E. Merwin, *Amer. J. Sci.*, 1919, [iv], **48**, 81; *A.*, 1919, ii, 401.

ated in detail, and the crystallised or glassy products examined with the petrographical microscope. The stability fields of the various compounds have been determined. It has been found that in many cases these compounds exist as more than one crystalline modification over different ranges of temperature; for example, four forms of calcium orthosilicate ($2CaO,SiO_2$) were recognised. Continuous series of mixed crystals, solid solutions with more or less limited degrees of miscibility, and various eutectics were

FIG. 2.



Compounds of the system CaO–MgO–Al_2O_3–SiO_2 plotted on a tetrahedron (shown in plan).

determined. An enormous mass of useful data has been accumulated. Here it is only possible to indicate the compounds that were observed under the conditions of the experiments. This may be done most concisely by means of a diagram (Fig. 2). Here, on the surface of the tetrahedron, the six edges represent the six possible binary systems, and the faces the four ternary systems, whilst the interior would represent the quaternary system CaO–MgO–Al_2O_3–SiO_2 itself. On the base of the tetrahedron, representing the system CaO–MgO–Al_2O_3, no compounds occur (nor do any in the binary system CaO–MgO). The three other

equilateral triangles meeting in the SiO_2-apex and representing the other ternary systems are of course foreshortened in the diagram. Partial systems lying within the tetrahedron that have been investigated, and mentioned in previous Reports, are diopside–anorthite, forsterite–anorthite, and åkermanite–gehlenite. Here no definite compounds have been recorded, but between åkermanite and gehlenite there is a complete series of mixed crystals.

In these experiments, the pure materials in known proportions were subjected to dry fusion at very high temperatures (from about 1,000° up to 2,800°, the melting point of magnesia). The conditions are thus not quite the same as those occurring in nature in the processes of rock formation. Here the element of time is of importance, whilst the presence of even small amounts of water under pressure must exert a profound influence. The diagram therefore tells only a part of the story, and it must not be taken to represent all the possible compounds or combinations of the four oxides. Several of the compounds shown have not been found in nature; on the other hand, some common minerals (for example, the amphiboles) are not represented. The compound $3CaO,Al_2O_3,3SiO_2$, well known as garnet (grossularite), is represented in the diagram by two tetragonal forms, one of which is near to sarcolite; and $2MgO,2Al_2O_3,5SiO_2$ shows some resemblances to cordierite.

In addition to the systems mentioned above, some other series of silicate fusions have been investigated in the Geophysical Laboratory at Washington. One of these deals with the complex melilite group of tetragonal minerals.[19] Tests were made on more than a hundred mixtures in various proportions of the compounds $2CaO,MgO,2SiO_2$ (åkermanite), $2CaO,Al_2O_3,SiO_2$ (gehlenite), $3CaO,Al_2O_3,3SiO_2$ (equivalent to grossularite), $3CaO,Fe_2O_3,3SiO_2$ (equivalent to andradite), $3Na_2O,Al_2O_3,3SiO_2$ ("lagoriolite," known only as an artificial preparation), and

$$9(3CaO,Al_2O_3,3SiO_2) + 1(3Na_2O,Al_2O_3,3SiO_2)$$

(sarcolite). Åkermanite is optically uniaxial with positive sign and refractive indices ω_{Na} 1·632 and ϵ_{Na} 1·639, whilst gehlenite is optically negative with ω_{Na} 1·669 and ϵ_{Na} 1·658. These two compounds form a complete series of mixed crystals in which the optical constants change gradually with the change in composition. Crystals of a certain intermediate composition (near 50 per cent. of each component) are optically isotropic for one or other colour of light. Mixed crystals are also common in other pairs of the compounds enumerated above and in mixtures of three or more of them, although in some cases the miscibility is not complete. The various products correspond more or less closely with the natural

[19] A. F. Buddington, *Amer. J. Sci.*, 1922, [v], **3**, 35; *A.*, ii, 155.

minerals gehlenite, åkermanite, melilite, humboldtilite, and sarcolite, the analyses of which are interpreted as mixtures of the molecules stated above. These tetragonal substances are also well known as constituents of the slags from iron furnaces; and åkermanite long since found in slags has only recently been recognised in volcanic rocks. The crystals present the appearance of regular cubes, owing to the equal development of a tetragonal prism with the basal planes; and they are interesting optically on account of their anomalous double refraction. The composition of some slag crystals recently investigated has been interpreted in quite another manner.[20] They are regarded as polysilicates, $R''_3Si_2O_7$, with some alumina present in solid solution, and the name "justite" has been applied to the group. Detailed determinations were made of the optical constants of these crystals.

Silicates of strontium and barium have been investigated in the Geophysical Laboratory.[21] In the system SrO–SiO_2, besides strontium oxide (cubic with perfect cubical cleavages) and forms of silica (tridymite and cristobalite) there are the metasilicate ($SrSiO_3$) and orthosilicate (Sr_2SiO_4). The metasilicate forms hexagonal crystals which are hemimorphic and twinned on the base, and are optically uniaxial and positive. It forms, however, a complete series of mixed crystals with the monoclinic pseudo-wollastonite (α-$CaSiO_3$), so that it is suggested that the crystals are really pseudo-hexagonal and monoclinic. The system BaO–SiO_2 gives several compounds, namely, $2BaO,SiO_2$ (granular), BaO,SiO_2 (orthorhombic), $2BaO,3SiO_2$, and $BaO,2SiO_2$, the last two being both orthorhombic and forming a complete series of mixed crystals. Whilst the system $CaSiO_3$–$SrSiO_3$ gives the series of mixed crystals mentioned above, the system $CaSiO_3$–$BaSiO_3$ gives the double compound $BaO,2CaO,3SiO_2$. With $MgSiO_3$, no compounds analogous to diopside are formed. Artificial strontium felspar, $SrO,Al_2O_3,2SiO_2$, analogous to anorthite, is probably triclinic; whilst $BaO,Al_2O_3,2SiO_2$ is monoclinic, corresponding with the mineral celsian. Different results have, however, been obtained for barium alumino-silicate by A. S. Ginzberg.[22] The thermal diagram of the system $CaAl_2Si_2O_8$–$BaAl_2Si_2O_8$ shows the melting point of anorthite at 1,400°, and of the barium compound at about 1,640°, a eutectic point at 1,323° with 50 per cent. of each component, and mixed crystals limited to 20 per cent. of $BaAl_2Si_2O_8$. The optic axial angle 2V diminishes from 80° for anorthite to 68°

[20] K. Hofmann-Degen, *Sitzungsber Heidelberger Akad. Wiss.*, 1919, Abt. A, Abh. 14.

[21] P. Eskola, *Amer. J. Sci.*, 1922, [v], **4**, 331; *A.*, 1922, ii, 849.

[22] Collection of Scientific Papers dedicated to F. Y. Levinson-Lessing, Petrograd, 1915. [*Min. Mag.* (*Abstr.*), 1923, **2**, 153.]

in the mixed crystals richest in barium, but the optical orientation is only slightly affected. Excess of $BaAl_2Si_2O_8$ crystallises out as hexagonal plates, which are optically uniaxial and positive, corresponding with nepheline. Fused mixtures of orthoclase and $BaAl_2Si_2O_8$ crystallise with difficulty, but with 15 per cent. $KAlSi_3O_8$ uniaxial crystals resembling the pure barium-nepheline were obtained. The compound $BaAl_2Si_2O_8$ therefore exists in three forms, namely, the hexagonal barium-nepheline, in mixed triclinic crystals with anorthite, and as the monoclinic celsian (also prepared artificially by P. Eskola). This is analogous to the corresponding sodium compound, $Na_2Al_2Si_2O_8$, which exists as the hexagonal soda-nepheline below 1,248° and as the triclinic felspar carnegieite up to the melting point 1,526°; although here the corresponding monoclinic form is not known.

In this connexion, mention may be made of the interesting observations of G. W. Morey and N. L. Bowen [23] on the melting point of potash-felspar. Previous observers had found the natural mineral to melt very sluggishly near 1,200°. Pure artificially-prepared orthoclase, after being maintained at this temperature for a week, presented the appearance of a glass, but when examined microscopically it showed skeletal optically-isotropic crystals embedded in a glass. At 1,400° the characteristic forms of leucite crystals were developed. The conclusion is drawn that potash-felspar ($KAlSi_3O_8$) has an incongruent melting point between 1,170° and 1,530°, due to the breaking down of the material into crystallised leucite and liquid, and that it is to be regarded as a binary compound in the system leucite–silica ($KAlSi_2O_6$–SiO_2). The same phenomenon was observed in experiments with natural orthoclases, but here the temperature limits vary with the impurities present.

The constitution of the various members of the zeolite group has been discussed at length by G. Tschermak,[24] and several new analyses are given. He finds that the ratio $Al : R'' + R'_2$ is in all cases 2 : 1, and that all zeolites can be represented by the formulæ $H_{2y}CaAl_2Si_xO_{2x+y+4}$ and $H_{2z}Na_2Al_2Si_zO_{2z+v+4}$. These contain a group, $CaAl_2Si_2O_8$ or $Na_2Al_2Si_2O_8$, equivalent to anorthite and soda-nepheline (or carnegieite), respectively, which is regarded as a nucleus ("Kern") and written *Kc* or *Kn* (also *Kb* and *Ks* for the corresponding barium and strontium nuclei). The various zeolites are regarded as compounds of one or other of these nuclei with a silicic acid, combined water, and water of crystallisation, which are

[23] *Amer. J. Sci.*, 1922, [v], **5**, 1; *A.*, 1922, ii, 577.

[24] *Sitzungsber. Akad. Wiss. Wien*, 1917, Abt. I, **126**, 541—606; 1918, Abt. I, **127**, 177—289; *A.*, 1921, ii, 703.

supposed to form a network enclosing the nucleus. Such a structure is regarded as offering an explanation of the variation of the optical characters of the zeolites with loss or gain of water, the various adsorption phenomena, and the ease with which the bases may be replaced. For example, natrolite is written as an orthosilicate with SiH_4 in combination, namely, $SiH_4Kn = H_4Na_2Al_2Si_3O_{12}$. Chabazite as a disilicate in combination with polysilicic acids (Si_2H_4, Si_4H_8, Si_2H_2, or SiH_4) and water, namely, $Si_2H_4KcO_2H_4$,2aq= $H_{12}CaAl_2Si_4O_{18}$; and gmelinite the same with *Kn* in place of *Kc*. (For further details see the abstract.)

Lengthy discussions have taken place as to the part played by water in zeolites.[25] The experiments of some authors suggest that dehydration and rehydration proceed in steps, corresponding to a series of definite hydrates, whilst other authors maintain that the process is continuous. A detailed account of Nova Scotian [26] zeolite localities includes many new analyses and dehydration curves.

A book by V. Iskyul on "Experimental Investigations in the Province of the Chemical Constitution of the Silicates. The Chlorites" has been published in Russian (Petrograd, 1917, 310 pp.).[27] This deals more especially with the group of the chlorites, but it also includes several other minerals—olivine, serpentine, garnet, amphibole, and pyroxene—which, by reason of their association in nature as alteration products, are usually regarded as having some bearing on the constitution of the chlorites. In the experiments, the minerals, both before and after ignition, are digested in 2·14 per cent. hydrochloric acid solution on the water-bath for two hours. The silica passing into solution is estimated, and also the precipitated silica that is extracted by sodium carbonate solution. The ratio of these two values is taken as the solubility of silicic acid in the mineral. This is plotted against the volume of the solvent expressed in c.c. per gram of the mineral altered (the former as ordinates and the latter as abscissæ), and the resulting curve is called the silica solubility curve. A large number of complete analyses are also given of the minerals employed in the experiments. Minerals of the olivine group behave as orthosilicates; but after ignition those containing iron yield some metasilicate: $Fe_2SiO_4 + O \longrightarrow Fe_2O_3 + SiO_2$ and $Mg_2SiO_4 + SiO_2 \longrightarrow 2MgSiO_3$. The serpentine minerals

[25] G. Stoklossa, *Jahrb. Min., Beil.-Bd.*, 1918, **42**, 1; F. Rinne, *Ber. Sächs. Akad. Wiss.*, 1920, **72**, 12; O. Weigel, *Sitzungsber. Ges. Naturwiss. Marburg*, 1920, 48; K. H. Scheumann, *Ber. Sächs. Akad. Wiss.*, 1921, **73**, 3; A. Beutell, *Centr. Min.*, 1921, 694, 721; O. Weigel, *ibid.*, 1922, 164, 201. [*Min. Mag.* (*Abstr.*), 1923, **2**, 57.]

[26] T. L. Walker and A. L. Parsons, *Univ. Toronto Studies, Geol. Ser.*, 1922, **14**, 13.

[27] *Min. Mag.* (*Abstr.*), 1924, **2**, 207.

are metasilicates; but whilst compact serpentine and chrysotile behave like the pyroxenes (enstatite), the antigorite variety reacts like the amphiboles (anthophyllite). On ignition, serpentine gives $H_4Mg_3Si_2O_9 \longrightarrow H_2O + Mg_2SiO_4 + MgSiO_3$. In the amphiboles and pyroxenes the solubility curves are approximately straight lines, but the silica solubility of the former is about twice that of the latter. Since the bulk composition is the same for both, the difference in behaviour may be due to polymerism or isomerism of the $(R''SiO_3)_n$ molecule. The solubility curves of silica in the chlorites are of three types: (1) lying very close to the abscissæ, as in penninite ($H_{22}R_{13}''R_4'''Si_8O_{46}$), tabergite ($H_{20}R_{12}''R_4'''Si_8O_{44}$), and rhodochrome ($H_{18}R_{11}''R_4'''Si_7O_{40}$); (2) the curve at first rising slowly, but much steeper in its later course, as in leuchtenbergite and clinochlore (both $H_{30}R_{17}''R_8'''Si_{10}O_{64}$); and (3) lying close to the ordinates, as in prochlorite ($H_{24}R_{14}''R_8'''Si_8O_{54}$) and corundophyllite ($H_{20}R_{11}''R_8'''Si_6O_{45}$). With increasing silica-content, as shown by the bulk-analyses of the chlorites, there is diminishing silica solubility. The experiments rather support Vernadsky's theory that the chlorites are salts, and complex compounds of these salts, of the acids $Al_2Si_{2+m}O_{7+2m-n}(OH)_{2n}$.

Some comparative experiments have been made by E. Norin [28] on the dissociation of the hydrous alumino-silicates, prehnite ($H_2O,2CaO,Al_2O_3,3SiO_2$), zoisite (orthorhombic $H_2O,4CaO,3Al_2O_3,6SiO_2$), and epidote (monoclinic $H_2O,4CaO,3Al_2O_3,6SiO_2$, with some iron replacing aluminium and calcium), in which the small percentage of water is expelled only at high temperatures. The finely powdered materials were heated for one hour at various definite temperatures and then boiled for twenty minutes in a 7 per cent. solution of hydrochloric acid. Lime, alumina, and ferric iron were estimated in the solution, and the separated silica extracted with a 5 per cent. soda solution. Prehnite is partly soluble in this strength of acid before ignition, and after ignition the amount dissolved is proportional to the water that has been expelled; finally it is completely soluble. In all cases, the amounts of lime, alumina, and silica dissolved are in the same ratio as in the original mineral. Zoisite is only slightly attacked before ignition. With loss of water a molecular change takes place and the material then passes into solution. Epidote also shows a progressive molecular change with the gradual loss of water between 940° and 1,100°. Here the alumino-silicate and the ferri-silicate dissociate independently of each other, suggesting that in one and the same silicate molecule ferric oxide does not isomorphously replace alumina.

[28] *China J. Sci. and Arts*, 1923, **1**, 390. [*Min. Mag.* (*Abstr.*), 1924, **2**, 215.]

The alumino-silicate nucleus, $H_2Al_2Si_2O_8$, evidently present in many silicates, is very stable, and it persists from the rock-forming minerals into many of their weathering products. By chemical means it can be broken down only by strong acids or at a high temperature. As pointed out by V. I. Vernadski,[29] it can, however, be broken down by certain organisms. That diatoms are able to extract silica from clay suspended in water has been long known, and the same action has given rise to the presence of free aluminium hydroxide in the Russian black-earths. A culture of bacteria and diatoms from pools near Kiev, when added to water free from silica but containing suspended kaolin, extracted silica for their growth with at the same time separation of free aluminium hydroxide. A somewhat analogous case is that shown in the extraction of potash from micas by growing plants. Comparative experiments [30] with peas and oats grown in water or pure quartz-sand and supplied with the necessary soluble inorganic salts, but in one set with the potash supplied as finely powdered biotite (K_2O 7·44 per cent.) or sericite (K_2O 5·14 per cent.), gave a more luxuriant growth with the micas, especially biotite, than with a soluble potash salt. With the decomposition of the biotite an alkaline reaction is produced. In this connexion, a long series of experiments has been made on the amount of potash extracted from various micas by prolonged action of acids (hydrochloric, citric, carbonic) and salt solutions.[31]

Some light on the constitution of silicates may be expected from a correlation of the various physical characters with variations in chemical composition in isomorphous series. It is necessary, however, that all the data [32] should be actually determined on the same sample of material—and not, as is often done, to quote a portion of the data from the literature for similar material from the same locality. The regular variation of the optical constants of the plagioclase felspars (albite, $NaAlSi_3O_8$, to anorthite, $CaAl_2Si_2O_8$) is, of course, well known, and in fact the composition of plagioclases in rock-sections is always deduced from their optical properties. Carefully determined data connecting the optical constants (refractive indices and optic axial angle) with the chemical composition are gradually being accumulated for some other groups of minerals. But usually the case is complicated by the presence of several variable components in the isomorphous mixture. For

[29] *Compt. rend.*, 1922, **175**, 450; *A.*, i, 1096.

[30] B. H. Cranner, *Norges Geol. Unders.*, 1922, No. **114**.

[31] V. M. Goldschmidt and E. Johnson, *Norges Geol. Unders.*, 1922, No. **108**.

[32] Such data are collected and tabulated in the "Tables annuelles de constantes et données numériques," vol. 4, for 1913—16 (Paris, 1921—22). The mineralogy chapter is issued as a reprint "Données numériques de cristallographie et de minéralogie," by L. J. Spencer (Paris, 1923).

example, in the olivine group [33] a first rough division must be made into the three series forsterite–fayalite, forsterite–tephroite, and tephroite–fayalite, and in the scapolite [34] and other groups there are several components. In the clinozoisite-epidote group, with increasing ferric iron the optic axial angle 2V measured over the negative bisectrix decreases, and the refractive index β increases, whilst the dispersion $2V_D - 2V_E$ is irregular. To explain these variations, F. Zambonini [35] has suggested that there are here two series of mixed crystals—a normal and an abnormal series. Writing the formula of clinozoisite as $Ca_2Al_2(AlOH)(SiO_4)_3$, he points out that the replacement of Al_2 or Al(OH), or both, by iron would give three series of stereoisomeric mixed crystals, which would be expected to differ in their physical characters. Similarly, the isomorphous replacement of calcium in apatite by, say, lead might give either $3Ca_3(PO_4)_2,(Ca,Pb)Cl_2$ or $3(Ca,Pb)_3(PO_4)_2$, $CaCl_2$. This is a suggestion that may bear fruit.

The method of tetrahedral plotting, as illustrated above in Fig. 2, was extensively employed by H. E. Boeke [36] [1881—1918], and since continued by his pupil W. Eitel,[37] for plotting the constituent oxides of mixed crystals. Large numbers of analyses of rock-forming minerals were collected from the literature and re-calculated as molecular percentages. For example, 336 analyses of hornblende are treated as representatives of the four-component systems, SiO_2–CaO–(Mg,Fe)O–$(Al,Fe)_2O_3$ (aluminous hornblendes) and SiO_2–RO–R_2O_3–R_2O (alkali-hornblendes), and the amounts of these oxides are plotted, in each case, from the four corners of a tetrahedron. A point inside the tetrahedron then represents the composition shown by each analysis, and its position is recorded by the co-ordinates of orthogonal projections on three rectangular planes. It is found that the analyses fall into certain groups and clusters. Five-component systems are plotted in four dimensions, and a seven-component system is plotted on a "six-dimensional heptatope." Much paper is filled and the reader is left bewildered.

Artificial Reproduction of Minerals.

Since the publication of P. N. Chirvinsky's "Reproduction artificielle de minéraux au xix^e siècle" (par P. Tchirwinsky, Kieff,

[33] H. Magnusson, *Geol. För. Förh.*, 1918, **40**, 601; *A.*, 1920, ii, 261.

[34] N. Sundius, *Bull. Geol. Inst. Univ. Upsala*, 1919, **16**, 96; *A.*, 1920, ii, 260.

[35] *Atti* (*Rend.*) *R. Accad. Lincei*, 1921, [v], **30**, (2), 80, 117, 162, 203.

[36] *A.*, 1916, ii, 570.

[37] *Jahrb. Min., Beil.-Bd.*, 1918, **42**, 173, 223; 1922, **47**, 201; see also *ibid.*, 1921, **44**, 369; 1921, **45**, 275; 1922, **45**, 311; *Z. Krist.*, 1921, **56**, 526.

1903—1906; in Russian) no systematic account of this subject has been given. P. Niggli has summarised the recent literature bearing on the synthesis of polymorphous minerals [38] and also that dealing with some dry silicate fusions.[39] He concluded that the production of the different modifications of the same chemical substance depends in most cases on variations in temperature rather than in pressure. Much work has now been done on the synthesis of numerous minerals, and there is material for a good book on the subject. Here only a few salient and recently published points can be touched upon.

The important experimental work done at the Geophysical Laboratory of the Carnegie Institution at Washington has dealt mainly with the dry fusion of silicate systems, which have been referred to above. Here mention may be made of some hydrothermal experiments. G. W. Morey and C. N. Fenner [40] have studied the system H_2O–K_2SiO_3–SiO_2 over a temperature range from 200° to 1,000°, and various potassium silicates have been determined, although none of them are known as minerals. By the addition of alumina and experimenting with the system K_2O–Al_2O_3–SiO_2–H_2O W. J. Müller and J. G. Koenigsberger [41] obtained more interesting results. The materials, sometimes with the addition of carbon dioxide, were heated in a bomb for several hours or days at 100° to 440°. The bomb contained a filtering device by means of which it was possible to collect crystals that had separated from the clear liquid. These were formed in only small amount and include zeolites, orthoclase, pectolite, quartz, and calcite. In the solid material at the bottom of the bomb there was found, in addition to the minerals just mentioned, also leucite, nepheline, and pyrophyllite. The zeolites include analcite, a micaceous zeolite related to gyrolite, and several new potassium zeolites; they commence to form below 100°, and are stable up to about 300°. Orthoclase is formed at 360° and with increasing temperature takes the place of leucite. In the presence of an excess of carbon dioxide at 310° only quartz is stable.

The system Fe_2O_3–SO_3–H_2O has been studied by E. Posnjak and H. E. Merwin [42] also in the Geophysical Laboratory. Ferric sulphate with various proportions of sulphuric acid and water was heated in sealed tubes for some days or months at 50° to 200°. In addition to iron hydroxides, nine sulphates were isolated and determined crystallographically and optically. Some of the products are stable only in contact with solutions of certain concentrations, temperatures,

[38] *Fortschr. Min. Krist. Petr.*, 1916, **5**, 131. [39] *Ibid.*, 1920, **6**, 35.
[40] *J. Amer. Chem. Soc.*, 1917, **39**, 1173; *A.*, 1917, ii, 370.
[41] *Z. anorg. Chem.*, 1918, **104**, 1; *A.*, 1918, ii, 402; J. G. Koenigsberger and W. J. Müller, *Jahrb. Min., Beil.-Bd.* 1921, **44**, 402; *A.*, 1921, ii, 459.
[42] *J. Amer. Chem. Soc.*, 1922, **44**, 1965; *A.*, 1922, ii, 772.

or pressures. But of the whole series so prepared only two were identified with known minerals, namely, orthorhombic

$$2Fe_2O_3,5SO_3,17H_2O,$$

identical with copiapite, and orthorhombic $Fe_2O_3,4SO_3,9H_2O$, identical with rhomboclase. On the other hand, several crystallised and well-defined ferric sulphates met with in nature were not obtained. Evidently nature has devised some other method, and very likely more than one, of dealing with the system Fe_2O_3–SO_3–H_2O. Experiments on the constitution and genesis of the natural ferric sulphates have been made by R. Scharizer since 1898, and his results described in a long series of papers. For the orthorhombic rhomboclase,[43] he writes the formula as $(FeOH)_2(HSO_4)_4 + 6H_2O$. Over concentrated sulphuric acid it loses $6H_2O$; and at 128° it passes into $(FeOH)_2(HSO_4)_4$, then $Fe(SO_4)(HSO_4)$, and finally $Fe_2(SO_4)_3$. The compound $(FeOH)_2(HSO_4)_4$ is deposited only from strongly acid solutions (containing at least 66·53 per cent. H_2SO_4); its crystals are pseudo-rhombohedral, consisting of three or six monoclinic individuals twinned together. The hexagonal metavoltine [44] has often been prepared artifically, although it is rare as a mineral. It is a salt of ferri-sulphuric acid, $H_4[(SO_4)_4(FeOH)_2]$, in which only part of the hydrogen is replaced by potassium; the water of crystallisation is variable with a maximum of $5H_2O$, and two other definite hydrates appear to exist. Several well-crystallised sulphates found in ancient (? Roman) workings in the Rio Tinto pyritic deposits have been described and analysed. In the same paper, H. F. Collins [45] records the results of numerous experiments on the crystallisation of mixed solutions of copper and ferrous sulphates in various proportions. In the monoclinic series of mixed crystals, $(Fe,Cu)SO_4,7H_2O$ (pisanite), it was found that the maximum amount of copper that can be taken up is 14·65 per cent. (= 65·95 per cent. $CuSO_4,7H_2O$); whilst in the triclinic series, $(Cu,Fe)SO_4,5H_2O$ (chalcanthite), the maximum amount of iron is only 0·84 per cent. (= 3·65 per cent. $FeSO_4,5H_2O$).

Various forms of calcium carbonate have been prepared by M. Copisarow.[46] At a temperature of 305° and pressure of 24 atmospheres he obtained calcite as a granular, crystalline aggregate, coherent enough to take a good polish and closely resembling marble.[47] At a lower temperature (1—5°) from solution feathery

[43] *Z. Krist.*, 1921, **56**, 353. [44] R. Scharizer, *ibid.*, 1923, **58**, 420.
[45] *Min. Mag.*, 1923, **20**, 32; *A.*, ii, 776. [46] *T.*, 1923, **123**, 785.
[47] This recalls the early experiments of Sir James Hall, which were commenced in 1790, and of which a good account has recently been given by J. S. Flett in an address, "Experimental Geology," at the British Association (Report for 1921, 1922, 56).

crystals of hydrocalcite were formed. These are stated to have the composition $CaCO_3,5H_2O$, and to become opaque through loss of water at 17—18°. They are no doubt identical with the mineral hydroconite, which was re-described in 1907 under the name lublinite with the same composition, $CaCO_3,5H_2O$. Better crystals, 1 cm. in length, have been obtained by J. E. Mackenzie [48] by the action of carbon dioxide on "sugar-lime" solution at 2°. In this case, the composition is given as $CaCO_3,6H_2O$. The clear crystals commence to lose water at 5°, changing into calcite; and dilatometric experiments do not indicate the existence of any intermediate hydrate. The latter result confirms that of Johnston, Merwin, and Williamson,[49] who also found only one hydrate, $CaCO_3,6H_2O$, the crystals of which are monoclinic.

The mode of formation of dolomite in nature has been much discussed and many attempts have been made to prepare it artificially. All attempts at the ordinary temperature and pressure have failed. Successful results have recently been obtained by A. E. Mitchell [50] in a special apparatus devised for working under pressures of carbon dioxide up to 20 atmospheres at a temperature of 25°. From mixed solutions of calcite and nesquehonite ($MgCO_3,3H_2O$) well-defined rhombohedra with the physical characters of dolomite were obtained.

Dissociation of Carbonates.

In connexion with the use of dolomite as a refractory material it has often been assumed that when heated the material first breaks down into magnesium oxide and calcium carbonate. This would imply either that dolomite is not a definite compound, $CaMg(CO_3)_2$, or that such a compound splits up into $CaCO_3$ and $MgCO_3$ before any evolution of carbon dioxide takes place. Recent experiments do not, however, confirm this. C. S. Garnett,[51] heating dolomite in a current of air at the ordinary pressure, determined the loss of carbon dioxide at various temperatures, and these plotted against one another give a continuous curve. The dissociation is slow between 500° and 675°, and is complete at 898°. As soon as dissociation had commenced, free calcium oxide was found to be present. Grecian magnesite ($MgCO_3$) under the same conditions showed vigorous dissociation from 540° with completion below 650°. Artificially prepared magnesium carbonate ("magnesia alba") is completely decomposed at about 430°. A. E. Mitchell [52] has

[48] *T.*, 1923, **123**, 2409.
[49] *Amer. J. Sci.*, 1916, [iv], **41**, 473; *A.*, 1916, ii, 433.
[50] *T.*, 1923, **123**, 1887.
[51] *Min. Mag.*, 1923, **20**, 54; *A.*, ii, 763.
[52] *T.*, 1923, **123**, 1055.

determined the dissociation pressures of magnesite, dolomite, and calcite, which plotted against the temperatures give continuous curves with dolomite (695 mm. at 832°) intermediate between magnesite (760 mm. at 756°) and calcite (761 mm. at 896°). F. H. Smyth and L. H. Adams,[53] in a study of the system CaO–CO_2, have determined the behaviour of calcite up to 1,390° and 1,000 atmospheres. The curve is a continuous one (for log p, the dissociation pressure, against $1/T$ a straight line) up to 1,240° and 30,000 mm. marking the eutectic point CaO–$CaCO_3$. The melting point of calcium carbonate, which persists as calcite, is about 1,339° at 779,000 mm. pressure. No evidence was obtained of an inversion from calcite into "α-$CaCO_3$" at 970° as recorded by H. E. Boeke (1912) and by Johnston, Merwin, and Williamson.[49] In this connexion it may be mentioned that calcite is now generally recognised by petrologists as a primary constituent of certain types of igneous rocks; and W. C. Brøgger [54] has applied the name carbonatites to magmatic carbonate rocks.

Pseudomorphs and Alteration of Minerals.

Minerals, although usually more stable than other substances, are constantly, through long periods of time, undergoing changes in the earth's crust. From a close study of their mutual associations and alterations much information of a chemical nature may be gained. The only books dealing specially with these matters are those of J. F. A. Breithaupt, "Die Paragenesis der Mineralien" (1849), and J. R. Blum, "Die Pseudomorphosen des Mineralreichs" (1843, with four supplements to 1879). The study of these important subjects was since then long neglected, but now a revival is setting in. A suggestive little pamphlet by W. Maucher, "Die Bildungsreihe der Mineralien" (Freiberg, 1914), dealt with the order of deposition of the various minerals in metalliferous veins; and J. Koenigsberger [55] has recorded in minute detail the associations, paragenesis, and habit of the crystals of minerals found in rock-crevices in Alpine regions. Many isolated facts are recorded in petrographical papers, and in the numerous recent papers on the metallographic method of examining opaque ores on polished surfaces. Various pseudomorphs have been described by H. Laubmann.[56]

P. P. Pilipenko in his Mineralogy of the Altai Mts., quoted above,[15] has made a detailed study of the pseudomorphs met with in the different zones of the mineral veins. In the sulpho-zone 31 minerals

[53] *J. Amer. Chem. Soc.*, 1923, **45**, 1167; *A.*, ii, 490.
[54] *Videnskaps. Skrifter, Kristiania*, 1921, No. 9 (for 1920).
[55] *Abh. Akad. Wiss. München*, 1917—19, **28**, Nos. 10—12.
[56] *Jahrb. Min.*, 1921, i, 15; 1921, ii, 35; 1922, i, 1.

have given rise to 112 pseudomorphs; in the sulphoxy-zone 17 minerals gave 29 pseudomorphs; and in the oxy-zone 42 minerals gave 116 pseudomorphs. According to their tendency to form pseudomorphs, the minerals are divided as inactive (giving no pseudomorphs), slightly active (giving 1 or 2 pseudomorphs), and active (giving more than 2). In the sulpho-zone, the numbers of such minerals are 14, 15, and 16, respectively; in the sulphoxy-zone, 5, 15, and 2; and in the oxy-zone, 9, 29, and 13. The inactive minerals of the sulpho-zone include mainly sulphides of Bi, Sb, As, sulpho-salts (with Bi, Sb, As) of Cu, Pb, Ag, and tellurium and uranium compounds. Simple sulphides are more active, in the increasing order: cinnabar and galena, chalcopyrite and sphalerite, pyrites and marcasite. Similarly, for gangue-minerals: barytes, fluorite, silica, carbonates. In the oxy-zone the order of increasing activity runs: smithsonite, cerussite, malachite, quartz and its varieties, pyrolusite, psilomelane, goethite and limonite, that is, in the order Zn, Pb, Cu, Si, Mn, Fe. Inactive or slightly active minerals in the oxy-zone are compounds of Bi, Cr, As, U, Mo, V, P. In each zone, the pseudomorphs are formed mainly at the expense of minerals in the same zone, a few from minerals belonging to the zone below, but none from minerals of a higher zone. The formation of pseudomorphs thus, as a rule, takes a definite course: for example, galena $\longrightarrow$ anglesite $\longrightarrow$ cerussite; sphalerite $\longrightarrow$ hemimorphite $\longrightarrow$ smithsonite; and pyrites $\longrightarrow$ jarosite $\longrightarrow$ limonite.

An interesting series of mineral changes has been described from the Mendip Hills in Somerset.[57] Little work has been done on the minerals of this ancient mining district, and the only analysis previously made is that by Berzelius in 1823, when he established the species mendipite. This mineral had, however, been found long before, and is mentioned in John Woodward's "Catalogue of English Fossils" (1728); he says:[58] ". . . Its whole Appearance is like that of a Spar, and nothing like Lead appears, tho' it be very rich of that Metal. . . ." The mendipite is found as nodules embedded in manganese oxide, the latter being much intermixed with calcite and occurring in limestone. It is usually more or less completely altered to carbonates, this change having evidently been brought about by the action of water containing calcium hydrogen carbonate in solution, and the chlorine removed as calcium

[57] L. J. Spencer, with analyses by E. D. Mountain, *Min. Mag.*, 1923, **20**, 67; *A.*, ii, 774.

[58] The specimen so described, together with several others from the Mendip Hills, is still preserved in the Woodwardian Collection at Cambridge. Woodward's Catalogue also records the results of some of his experiments made on "Bodyes digg'd up out of the Bowels of the Earth," Some of the specimens were given to him by his contemporary, Sir Isaac Newton.

chloride. The first step in the change was to hydrocerussite,[59] and not, as might have been expected, to the chloro-carbonate phosgenite ($PbCO_3,PbCl_2$). Analyses of the pure hydrocerussite show, however, the presence of a small amount of chlorine isomorphously replacing hydroxyl, thus suggesting the existence of a compound $2PbCO_3,PbCl_2$. With further alteration the hydrocerussite changes to cerussite, and some distinct pseudomorphs of cerussite after rhombohedral crystals of hydrocerussite have been found. The nodules of mendipite thus come to be surrounded by zones of alteration products as represented diagrammatically in Fig. 3, the changes having proceeded in the direction :

Mendipite ($2PbO,PbCl_2$) ⟶ Hydrocerussite ($2PbCO_3,Pb(OH)_2$) ⟶ Cerussite ($PbCO_3$)

Fig. 3.

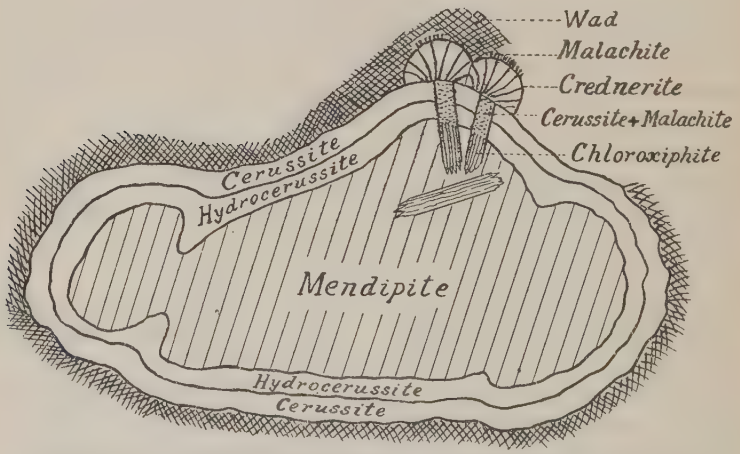
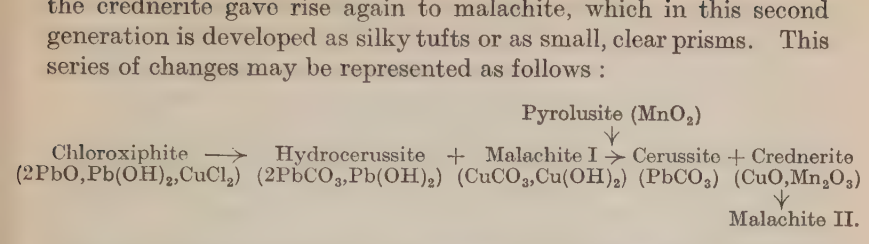


Diagram to represent the alteration products of Mendipite and Chloroxiphite.

Occasionally embedded in the mendipite are green, monoclinic blades of a new mineral, chloroxiphite, an oxychloride of lead and copper. In the alteration zone, this is represented by a compact granular mixture of malachite with hydrocerussite or cerussite, and pseudomorphous forms are sometimes shown (Fig. 3). As a later alteration by interaction with the surrounding manganese dioxide, the mineral crednerite (CuO,Mn_2O_3) was developed as fan-shaped aggregates of black scales on the surface of the nodules. Still later,

[59] Hydrocerussite, hitherto found very sparingly as a mineral, is identical with " white lead " (*cerussa*), and its formula was based on analyses made of the artificial product. Large crystals in the Woodwardian Collection were mentioned in 1728 as : " They appear like Talc ; but are very ponderous, and doubtless hold Lead."

the crednerite gave rise again to malachite, which in this second generation is developed as silky tufts or as small, clear prisms. This series of changes may be represented as follows :


Pyrolusite (MnO_2)
Chloroxiphite ⟶ Hydrocerussite + Malachite I → Cerussite + Crednerite
($2PbO,Pb(OH)_2,CuCl_2$) ($2PbCO_3,Pb(OH)_2$) ($CuCO_3,Cu(OH)_2$) ($PbCO_3$) (CuO,Mn_2O_3)
Malachite II.

A second type of alteration is suggested by the presence of pseudomorphs of diaboleite (another new oxychloride of lead and copper as sky-blue, tetragonal crystals) after chloroxiphite, namely :

$$\underset{(2PbO,Pb(OH)_2,CuCl_2)}{\text{Chloroxiphite}} \longrightarrow \underset{(2Pb(OH)_2,CuCl_2)}{\text{Diaboleite}} + \underset{(2PbCO_3,Pb(OH)_2)}{\text{Hydrocerussite}}$$

The diaboleite is a more stable form and still persists in the cerussite zone. As to the origin of the mendipite itself, which appears to be really foreign to the deposit of manganese ore, it is suggested that lumps of galena derived from veins in the Carboniferous Limestone were deposited with the Dolomitic Conglomerate (a beach deposit surrounding the limestone hill), and that by the action of sea-water the lead sulphide was converted into oxychloride.

X-Ray Examination of Minerals.

When *X*-ray methods were introduced, the crystals first examined were those of simple minerals, and the early quantitative data obtained by the Braggs formed the basis of later work. More recently, the method has been extended to the examination of crystals of complex carbon compounds, and also to the structure of the atom itself. The positions of the spots and bands on the photographic films are evidently often open to more than one interpretation, and afford ample scope for speculation and controversy.

Two applications, however, of the *X*-ray methods may perhaps come to be of practical use in the determination of minerals; these are :

(1) *X*-ray qualitative (and quantitative) spectrum-analysis.

(2) Recognition of mineral-species in intimate mixtures.

The first of these depends on the known *X*-ray spectra of the elements.[63] In A. Hadding's [64] apparatus a few grains or powder of the mineral to be tested are placed on the copper or iron anti-

[63] D. Coster, *Chem. News*, 1923, **127**, *A.*, ii, 648.

[64] "De Röntgenkristallografiska apparaterna och deras användning," Lund, 1921; *Handl. Ingen. Vetensk. Akad. Stockholm*, 1922, no. 11; *Z. anorg. Chem.*, 1922, **122**, 195; *A.*, 1922, ii, 780.

cathode of the *X*-ray vacuum-tube and bombarded at a tension of 30,000 to 40,000 volts. The *X*-ray tube is constructed entirely of metal (except for the insulating parts) and is provided with a window of aluminium-foil opposite the anticathode. The spectrograph is a small disk-shaped box with a slit at the side and carrying a crystal plate mounted on a central axis; at the circumference is a photographic film. The rays emitted by the elements present in the mineral are analysed by the crystal grating of known dimensions (such as rock-salt), and their wave-lengths are given by the well-known equation $n\lambda = 2d \sin \theta$. The spectra show only few, easily recognisable lines, and their intensities indicate roughly the amount present of each element. In fluocerite Hadding detected, in addition to cerium and yttrium earths, the element with atomic number 61; and in cassiterite he detected germanium.[65] Using a modification of Hadding's spectrograph in which the rock-salt crystal is turned by clockwork, V. M. Goldschmidt and L.Thomassen[66] recognised the presence of element 72 (hafnium) together with zirconium in malacon and alvite from Norway. The formula of alvite they write as $(Zr,72,Th)O_2,SiO_2$. D. Coster [63] has estimated about 5 per cent. of hafnium in a zirconium mineral from the Urals, and about 2 per cent. in one from Brazil.

In Siegbahn's [67] apparatus a long-surface anticathode gives a divergent sheaf of rays of about 40° angle through the aluminium window of the metal *X*-ray vacuum-tube. Close to the slit is a fixed crystal plate which reflects the rays on to a photographic film. Between the angles 10° and 50° a calcite plate (with $2d = 6{\cdot}060$ Å.) will reflect wave-lengths 1·0 to 4·6 Å., and a gypsum plate (with $2d = 15{\cdot}15$ Å.) provides for wave-lengths 2·6—11·6 Å. This embraces all the elements from sodium to uranium which are charted for the two crystal plates. The simple spectra yielded by the small amount of substance placed on the anticathode are laid alongside the charts and the characteristic lines are quickly identified.

A second application of *X*-ray methods that has been suggested is for the recognition of the minerals present in intimate mixtures, such as fine-grained rocks, ores, clays, soils, etc. The material is examined by the powder method, using monochromatic rays of known wave-length, and the spectrum is compared with a standard set of spectra obtained under the same conditions with known minerals. By this method A. Hadding [68] has recognised the presence

[65] A. Hadding, *Z. anorg. Chem.*, 1922, **123**, 171; *A.*, 1922, ii, 855.

[66] *Norsk Geol. Tidsskrift*, 1923, **7**, 61; *A.*, ii, 174.

[67] M. Seigbahn, A. E. Lindh, and N. Stensson, *Z. Physik*, 1921, **4**, 61; *A.*, 1921, ii, 344.

[68] *Z. Krist.*, 1923, **58**, 108.

of quartz, muscovite, and kaolinite in various clays. His attempts to apply the method for the discrimination of the felspars in rocks were, however, without success.[69]

New Minerals.

Hasty work for the sake of priority unfortunately leads to the publication of many ill-defined species. Many papers, here as elsewhere, instead of helping in the advancement of science, are only an encumbrance and swell the overwhelming flood of scientific literature, which threatens to defeat its own ends and adds to the congestion of libraries. Editors as well as authors have still to realise that it is quality rather than quantity that will have a permanent value. In this place it is not possible to give a full list of so-called new minerals,[70] and a critical selection must be made. A few earlier more distinctive species are also included to fill the gap in these Reports between 1913 and 1922.

A heavy crop of radioactive minerals recorded from the recently-discovered deposits of uranium ore in the Katanga district of the Belgian Congo includes the new names becquerelite, chinkolobwite,[71] curite, dewindtite, kasolite, parsonsite,[72] schoepite,[73] soddite, and stasite. Some of these were referred to in the last Report, and two of the more certain are listed below. They all represent secondary alteration products (uranates, phosphates, silicates, and carbonates) of pitchblende, and they occur minutely crystallised and intimately intermingled. It is evident that the analyses have not always been made on ideally pure material, nor is it certain that the optical and other physical characters have in all cases been determined on the same kind of material as that used for analysis.

Akrochordite,[74] basic arsenate of manganese and magnesium, $Mn_3As_2O_8$,MnOH,MgOH,$5H_2O$, found as reddish-brown, wart-like aggregates in manganese ore at Långban, Sweden. The optical characters suggest monoclinic symmetry.

Ambatoarinite,[75] basic carbonate of strontium and cerium metals, $5SrCO_3$,$4(Ce,La,Di)_2(CO_3)_3$,$(Ce,La,Di)_2O_3$, occurring as colourless grains (orthorhombic) with celestite, monazite, etc., as a constituent of a crystalline limestone (marble) at Ambatoarina, Madagascar.

[69] *Lunds Univ. Årsskrift*, 1921, **17**, No. 6.

[70] Dictionary lists of new mineral names are given by L. J. Spencer at the end of each volume of the *Mineralogical Magazine*.

[71] A. Schoep, *Bull. Soc. Belge Géol.*, 1923, **33**, 87; *Bull. Soc. Chim. Belg.*, 1923, **32**, 345; *A.*, ii, 870.

[72] A. Schoep, *Compt. rend.*, 1923, **176**, 171; *A.*, ii, 174.

[73] T. L. Walker, *Amer. Min.*, 1923, **8**, 67.

[74] G. Flink, *Geol. För. Förh.*, 1922, **44**, 773.

[75] A. Lacroix, *Bull. Soc. franç. Min.*, 1916, **38** (for 1915), 265; *A.*, 1916, ii, 569.

Argentojarosite,[76] a variety of jarosite containing silver (19 per cent.) in place of potassium, $Ag_2[Fe(OH)_2]_6(SO_4)_4$, and analogous to the lead-bearing plumbojarosite. It forms a mass of minute, yellow to brown, hexagonal and optically uniaxial scales, and has been found at Dividend, Utah, in sufficient quantity to be used as an ore of silver. Apart from the very doubtful record of silver carbonate ("selbite") by C. J. Selb in 1794 and the oxychlorides of the percylite-boleite group, this is the only silver mineral containing oxygen.

Armangite,[77] manganese arsenite, $Mn_3(AsO_3)_2$, as black, rhombohedral crystals from Långban, Sweden. Arsenates are frequent as minerals, but arsenites are uncommon.

Camsellite,[78] hydrated magnesium borate, $Mg_2B_2O_5,H_2O$, forming white, fibrous masses intermixed with chrysotile and dolomite in serpentine from British Columbia. The optical characters indicate orthorhombic symmetry.

Chloroxiphite,[79] a lead copper oxychloride, $2PbO,PbCl_2,Cu(OH)_2$, occurring sparingly as green, bladed crystals (hence the name) embedded in mendipite [$2PbO,PbCl_2$] from the Mendip Hills, Somerset. The crystals are monoclinic and in many of their characters show a resemblance to epidote.

Cornetite, a basic copper phosphate, $2Cu_3(PO_4)_2,7Cu(OH)_2$, or perhaps $Cu_3(PO_4)_2,3Cu(OH)_2$, as minute, peacock-blue, orthorhombic crystals. It was first described by G. Cesàro [80] in 1912 as a copper cobalt phosphate from Katanga, and was later named cornetite.[81] More recently it was found in a neighbouring district in Northern Rhodesia,[82] analysis of this material giving the above formula with the absence of cobalt. A re-examination [83] of the Katanga material showed the presence of cobalt only as an impurity, and not in the pure crystals. Lastly, G. Cesàro,[84] writing the formula as $(CuOH)_3PO_4$, points out that this compound is dimorphous, being orthorhombic with optic axial angle $2E = 55°$ in cornetite, and monoclinic with $2E = 95°$ in pseudomalachite.

[76] W. T. Schaller, *J. Washington Acad. Sci.*, 1923, **13**, 233, named argentojarosite in a preliminary note in June. Also, in July, independently named argentojarosite by C. A. Schempp, *Amer. J. Sci.*, 1923, [v], **6**, 73; *A.*, ii, 503.

[77] G. Aminoff and R. Mauzelius, *Geol. För. Förh.*, 1920, **42**, 301; *A.*, 1921, ii, 269.

[78] H. V. Ellsworth and E. Poitevin, *Trans. Roy. Soc. Canada*, 1921, [iii], **15**, sect. IV, 1; *A.*, 1922, ii, 304.

[79] L. J. Spencer, *Min. Mag.*, 1923, **20**, 67; *A.*, ii, 774.

[80] *Ann. Soc. Géol. Belg.*, 1912, **39**, Bull. 241; *A.*, 1920, ii, 441.

[81] H. Buttgenbach, "Les Minéraux et les Roches," Liége, 1916, 452.

[82] A. Hutchinson and A. M. Macgregor, *Min. Mag.*, 1921, **19**, 225; *A.*, 1921, ii, 701.

[83] A. Schoep, *Min. Mag.*, 1922, **19**, 301; *A.*, 1922, ii, 219.

[84] *Ann. Soc. Géol. Belg.*, 1922, **45**, Bull. 102.

Creedite,[85] hydrated calcium aluminium fluoride and sulphate, $2CaF_2,2Al(F,OH)_3,CaSO_4,2H_2O$, as white radiating masses of monoclinic crystals with fluorite near Creede in Colorado. It has been further studied by W. F. Foshag,[86] who writes the formula $3CaF_2,Al(OH,F)_2SO_4,2H_2O$.

Curite,[87] hydrated lead uranate, $2PbO,5UO_3,4H_2O$, occurring with kasolite as orange-yellow, acicular crystals in Katanga. The needles give straight optical extinction with positive elongation.

Diaboleite,[79] lead copper oxychloride, $2Pb(OH)_2,CuCl_2$, or $Pb(OH)_2,PbCl_2,Cu(OH)_2$, found sparingly with choroxiphite embedded in mendipite from the Mendip Hills, Somerset. The minute, sky-blue crystals are tetragonal with characters similar to those of minerals of the percylite-boleite group [near $Pb(OH)_2,CuCl_2$, and sometimes containing also silver], but, as shown on analysis by E. D. Mountain, with different molecular ratios and much higher density (6·412, against 4·77—5·25).

Dixenite,[88] manganese arsenite and silicate,

$$(MnOH)_2Mn_3(SiO_3)(AsO_3)_2,$$

as rhombohedral scales in hæmatite at Långban, Sweden. The black scales are red by transmitted light. The combination of arsenite with silicate is unusual.

Finnemanite,[89] lead chloro-arsenite, $3Pb_3(AsO_3)_2,PbCl_2$, or $Pb_5Cl(AsO_3)_3$, as black, hexagonal prisms [$a : c = 1 : 0{\cdot}6880$] on hæmatite iron-ore at Långban, Sweden. It resembles mimetite in its general characters, but it is a chloroarsenite rather than a chloro-arsenate.

Germanite,[90] a massive, dark reddish-grey mineral containing 6·20 per cent. of germanium, together with copper and iron as sulphides. It occurs in some quantity intimately intermixed with zinciferous tennantite at Tsumeb, South-West Africa.

Hewettite,[91] hydrated calcium vanadate, $CaO,3V_2O_5,9H_2O$, or $CaH_2V_6O_{17},8H_2O$, forming mahogany-red, silky aggregates of orthorhombic needles, and occurring as an oxidation product of patronite at Minasragra, Peru. An isomeric form, also orthorhombic, but differing in its behaviour during dehydration, is called *metahewettite*. The latter is found as a dark-red, powdery impregnation in sandstone in Colorado and Utah.

[85] E. S. Larsen and R. C. Wells, *Proc. Nat. Acad. Sci.*, 1916, **2**, 360.
[86] *Proc. U.S. Nat. Mus.*, 1921, **59**, 419.
[87] A. Schoep, *Compt. rend.*, 1921, **173**, 1186; *A.*, 1922, ii, 77.
[88] G. Flink, *Geol. För. Förh.*, 1920, **42**, 436; *A.*, 1921, ii, 268.
[89] G. Aminoff, *Geol. För. Förh.*, 1923, **45**, 160.
[90] O. Pufahl, *Metall u. Erz*, 1922, **19**, 324.
[91] W. F. Hillebrand, H. E. Merwin, and F. E. Wright, *Proc. Amer. Phil. Soc.*, 1914, **8**, 33; *Z. Kryst. Min.*, 1914, **54**, 209; *A.*, 1915, ii, 271.

Inyoite,[92] hydrated calcium borate, $Ca_2B_6O_{11},13H_2O$, found as large, colourless, monoclinic crystals in the borate deposits of Inyo Co., California, and later in the gypsum mines at Hillsborough, New Brunswick.[93] Pseudomorphs of meyerhofferite [$Ca_2B_6O_{11},7H_2O$] and colemanite [94] [$Ca_2B_6O_{11},5H_2O$] after inyoite, evidently produced by the arid climate, are commonly found in California.

Kasolite,[95] hydrated uranium lead silicate, $3UO_3,3PbO,3SiO_2,4H_2O$, as radiating groups of ochre-yellow, monoclinic crystals from Kasolo, Katanga, Belgian Congo. Further crystallographic and optical data are given by H. Buttgenbach.[96]

Katoptrite,[97] manganese, aluminium, etc., silico-antimonate, $14(Mn,Mg,Fe)O,2(Al,Fe)_2O_3,Sb_2O_5,2SiO_2$, found as tabular, monoclinic crystals with magnetite iron-ore at Nordmark, Sweden. It is black with a brilliant metallic lustre and perfect micaceous cleavage. The brittle cleavage flakes are red and strongly pleochroic. It is possibly identical with the incompletely described hematostibiite.

Leifite,[98] a highly acidic fluosilicate, $Na_4(AlF)_2Si_9O_{22}$, as colourless, hexagonal prisms in alkali-pegmatite from Greenland.

Margarosanite,[99] lead calcium metasilicate, $PbCa_2(SiO_3)_2$, forming colourless, platy masses with perfect pearly cleavage, from Franklin Furnace, New Jersey. It was afterwards found in some quantity as snow-white columnar masses weighing up to 1 kilo. and as anorthic crystals at Långban, Sweden.[1]

Meyerhofferite,[2] hydrated calcium borate, $Ca_2B_6O_{11},7H_2O$, occurring as colourless, triclinic crystals or as a white, fibrous alteration product of inyoite (*q. v.*) from California.

Minasragrite,[3] hydrated vanadium sulphate, $V_2O_4,3SO_3,16H_2O$, or $V_2O_2H_2(SO_4)_3,15H_2O$. It is abundant at Minasragra, Peru, as an alteration product of the patronite ore, and it grows as a blue efflorescence on museum specimens of patronite. It is readily

[92] W. T. Schaller, *J. Washington Acad. Sci.*, 1914, **4**, 355; *Bull. U.S. Geol. Survey*, 1916, **610**, 35; *A.*, 1916, ii, 628.

[93] E. Poitevin and H. V. Ellsworth, *Bull. Geol. Survey, Canada*, 1921, **32**.

[94] A. F. Rogers, *Amer. Min.*, 1919, **4**, 135.

[95] A. Schoep, *Compt. rend.*, 1921, **173**, 1476; *A.*, 1922, ii, 155.

[96] *Bull. Acad. roy. Belg.*, 1922, 573.

[97] G. Flink, *Geol. För. Förh.*, 1917, **39**, 426; *A.*, 1919, ii, 112.

[98] O. B. Bøggild, *Medd. om Grønland*, 1915, **51**, 427; *Z. Kryst. Min.*, 1920, **55**, 425; *A.*, 1917, ii, 147.

[99] W E. Ford and W. M. Bradley, *Amer. J. Sci.*, 1916, [iv], **42**, 159; *A.*, 1916, ii, 532.

[1] G. Flink, *Geol. För. Förh.*, 1917, **39**, 438; *A.*, 1917, ii, 112.

[2] W. T. Schaller, *J. Washington Acad. Sci.*, 1914, **4**, 355; *Bull. U.S. Geol. Survey*, 1916, **610**, 35; *A.*, 1916, ii, 628.

[3] W. T. Schaller, *J. Washington Acad. Sci.*, 1915, **5**, 7; 1917, **7**, 501; *A.*, 1917, ii, 575.

soluble in cold water. The optical characters suggest monoclinic or triclinic symmetry.

Pascoite,[91] hydrated calcium vanadate, $2CaO,3V_2O_5,11(?)H_2O$, occurring as an orange-yellow powdery efflorescence on vanadium ores at Minasragra, Peru.

Phosphophyllite,[4] hydrated sulphato-phosphate of ferrous iron, magnesium, calcium, potassium, and aluminium,

$$3R_3P_2O_8,2AlOHSO_4,9H_2O,$$

forming colourless or pale green, monoclinic crystals with a perfect micaceous cleavage, and occurring with various other phosphates in pegmatite at Hagendorf, Bavaria.

Pyrobelonite,[5] hydrated lead manganese vanadate,

$$4PbO,7MnO,2V_2O_5,3H_2O,$$

found as fire-red, needle-shaped, orthorhombic crystals in manganese ore at Långban, Sweden.

Searlesite,[6] hydrated sodium borosilicate, $NaB(SiO_3)_2,H_2O$, occurring as small, white spherules of radiating fibres (probably monoclinic) in clay at Searles Lake, California.

Spencerite,[7] hydrated basic zinc phosphate,

$$Zn_3(PO_4)_2,Zn(OH)_2,3H_2O,$$

forming pearly-white, scaly cleavage-masses and small monoclinic crystals. It was found in some abundance as large stalactites in a cavern near Salmo, British Columbia, and most of the material was sent to the smelter before its nature was recognised. The dehydration curve [8] shows that three-fourths of the water is lost between 100° and 135°, giving a product corresponding chemically but not optically with tarbuttite $[Zn_3(PO_4)_2,Zn(OH)_2]$.

Trevorite,[9] nickel ferric-iron oxide or nickel ferrate, $NiFe_2O_4$, presumably belonging to the spinel group. It is found as a massive, black and opaque, strongly magnetic mineral in the Transvaal. It has been regarded as a doubtful species, but a re-examination by T. L. Walker [10] proves the material to be homogeneous.

Trigonite,[88] lead manganese hydrogen arsenite, $Pb_3MnH(AsO_3)_3$,

[4] H. Laubmann and H. Steinmetz, *Z. Kryst. Min.*, 1920, **55**, 566; *A.*, 1920, ii, 697.

[5] G. Flink, *Geol. För. Förh.*, 1919, **41**, 433; *A.*, 1920, ii, 442.

[6] E. S. Larsen and W. B. Hicks, *J. Washington Acad. Sci.*, 1914, **4**, 397; *Amer. J. Sci.*, 1914, [iv], **38**, 437; *A.*, 1914, ii, 851.

[7] T. L. Walker, *Min. Mag.*, 1916, **18**, 76; *A.*, 1916, ii, 629. A. H. Phillips, *Amer. J. Sci.*, 1916, [iv], **42**, 275; *A.*, 1916, ii, 569. T. L. Walker, *J. Washington Acad. Sci.*, 1917, **7**, 456; *Univ. Toronto Studies, Geol. Ser.*, 1918, **10**, 5; *A.*, 1919, ii, 71.

[8] T. L. Walker and A. L. Parsons, *Univ. Toronto Studies, Geol. Ser.*, 1921, **12**, 58.

[9] A. F. Crosse, *J. Chem. Met. Soc. S. Africa*, 1921, **21**, 126.

[10] *Univ. Toronto Studies, Geol. Ser.*, 1923, **16**, 53.

as sulphur-yellow crystals with the form of triangular wedges and of domatic-monoclinic symmetry. It is found with native lead in dolomite at Langban, Sweden.

Tungstenite,[11] tungsten sulphide, WS_2, forming feathery flakes resembling molybdenite [MoS_2] or graphite in appearance and occurring in a compact ore from Utah.

Ultrabasite,[12] an ultrabasic sulpho-salt, $Sb_4Ag_{22}Pb_{28}Ge_3S_{53}$, containing 2·20 per cent. of germanium. The orthorhombic crystals are black with metallic lustre and came from Freiberg, Saxony. The material had been found in an old English collection of minerals.

Vauxite,[13] hydrated ferrous-iron aluminium phosphate,

$$4FeO,2Al_2O_3,3P_2O_5,24H_2O + 3H_2O,$$

occurring as sky-blue, triclinic plates with wavellite and tin ore from Bolivia. Associated with it is *paravauxite*, with nearly the same composition, namely, $5FeO,4Al_2O_3,5P_2O_5,26H_2O + 21H_2O$, which forms colourless, triclinic prisms.

Villamaninite,[14] a disulphide, $(Cu,Ni,Co,Fe)S_2$, containing also some selenium (1·5 per cent.), occurring abundantly as small, black, cubic crystals and as nodular aggregates in crystalline dolomite near Villamanin, Spain. E. Thomson [15] from a microscopical examination of polished surfaces suggests that it is a mixture of two undetermined minerals, but the original material was definitely crystallised.

Weinschenkite,[16] hydrated phosphate of rare-earths,

$$(Er,Y)PO_4,2H_2O,$$

found as spherules and tufts of silky-white needles on limonitic iron-ore near Amberg, Bavaria. The name weinschenkite [17] has also recently been applied to a variety of hornblende.

Mention may here be made of three naturally-occurring crystallised carbon compounds to which mineralogical names have recently been applied :

Flagstaffite [18] = terpin hydrate, $C_{10}H_{20}O_2,H_2O$, as colourless,

[11] R. C. Wells and B. S. Butler, *J. Washington Acad. Sci.*, 1917, **7**, 596; *A.*, 1918, ii, 46.

[12] V. Rosický and J. Štěrba-Böhm, *Rozpr. České Akad.*, 1916, **25**, no. 45; *Z. Kryst. Min.*, 1920, **55**, 430; *A.*, 1920, ii, 696.

[13] S. G. Gordon, *Proc. Acad. Nat. Sci. Philadelphia*, 1923, **75**, 261; *A.*, ii, 646.

[14] W. R. Schoeller and A. R. Powell, *Min. Mag.*, 1920, **19**, 14; *A.*, 1920, ii, 256.

[15] *Univ. Toronto Studies, Geol. Ser.*, 1921, **12**, 39.

[16] H. Laubmann *in* F. Henrich, *Ber.*, 1922, **55** B, 3013; *A.*, 1922, ii, 860.

[17] G. Murgoci, *Compt. rend.*, 1922, **175**, 428.

[18] F. N. Guild, *Amer. Min.*, 1920, **5**, 169, 1921, **6**, 133; *A.*, 1921, ii, 51, 1922, ii, 76.

orthorhombic crystals found with resin in the radial cracks of pine-tree logs that had been buried for at least 500 years near Flagstaff in Arizona.

Hoelite [19]= anthraquinone, $C_{14}H_8O_2$, as delicate needles formed, together with sulphur and sal-ammoniac, by the burning of a coal seam in Spitsbergen.

Simonellite,[20] $C_{15}H_{20}$, as a white, crystalline (orthorhombic) encrustation on lignite from Tuscany.

Some Recent Books of Reference.

Fedorov's long-delayed "Tables of the Crystal Kingdom" [21] has at last appeared, being dated 1920, but only recently has a copy reached this country. Some account of this work has already been given by T. V. Barker in these Reports as long ago as 1913 (**10**, 247; **11**, 248). It is issued by the Russian Academy of Sciences and forms a quarto volume of 1,124 pages with an atlas of 213 plates. The crystallographic constants that have been determined for all known crystallised substances, including minerals, are systematically tabulated according to a special plan devised by the author. By measuring on the goniometer the angles included between the faces of an unknown crystal and reducing the results to the Fedorov elements, it is possible to identify the substance (in case it has been previously determined crystallographically) by reference to the tables. Such a method of crystallo-chemical analysis is practicable when only a small amount of material is available for determination, and the material is not thereby damaged or destroyed. Fedorov's methods are somewhat difficult to follow and are not generally known; but here we have a notable first attempt to reduce to some order the enormous and tangled mass of published crystallographic data. T. V. Barker [22] has estimated the number of crystallised substances dealt with in the work at 7,400, for 600 of which, however, the elements are not sufficiently precise, leaving 6,800 that have been completely determined. The percentages of these represented in the various systems are: cubic 7, tetragonal 5, hexagonal 3, rhombohedral 4, orthorhombic 23, monoclinic 46, anorthic 12 per cent. This total corresponds approximately with the number of crystallised substances, about 7,350, dealt with in P. Groth's well-

[19] I. Oftedal, "Resultater av de Norske Statsunderstøttede Spitsbergen-ekspeditioner" (*Videnskapsselskapet, Kristiania*), 1922, **1**, no. 3.

[20] G. Boeris, *Rend. Accad. Sci. Ist. Bologna*, 1919, **23**, 87. R. Ciusa and A. Galizzi, *Gazzetta*, 1921, **51**, (i), 55; *A.*, 1921, ii, 343.

[21] E. von Fedorow, unter Mitwirkung von D. Artemiev, Th. Barker, B. Orelkin, und W. Sokolow, "Das Krystallreich; Tabellen zur krystallo-chemischen Analyse," *Mém. Acad. Sci. Russie*, [viii], **36**, Petrograd, 1920.

[22] Note on E. S. Fedorov in *Min. Mag.* (*Abstr.*), 1923, **2**, 100.

known "Chemische Krystallographie" (5 vols., Leipzig, 1906—1919), where a chemical arrangement is adopted.

Another large crystallographic work of reference is Victor Goldschmidt's "Atlas der Krystallformen" (Heidelberg, 1913—1923), comprising nine volumes of text and plates, in all eighteen quarto volumes. Here only minerals are taken into account, these being arranged alphabetically according to species. The idea has been to collect from the literature all published geometrical figures of crystals. For example, 2,692 figures of calcite crystals, 855 of quartz, and 691 of pyrites have been brought together for comparison and reference. In all, there are about 1,600 plates showing about 30,000 figures—a truly German production. In the text are tabulated the symbols and indices used by different authors for the several crystal-forms of each species. Detailed references are given to the literature, from which also long lists of errata have been collected. We fear that some at least of these errata have been caused by the confusion introduced by Goldschmidt himself into crystallographic notation. He has even thought it necessary to change the letters, indices, and axes of reference of calcite, and in his different works two distinct systems are made use of (distinguished as "G_1" and "G_2"). Surely the old-fashioned and well-established $r(100)$ of Miller or $r(10\bar{1}1)$ of Dana is quite good enough to express the cleavage-form of calcite. The selection of an orientation and parameters for a crystal is in any case more or less arbitrary, and, unless the original describer is proved to be quite wrong, nothing is gained (only confusion) by introducing a change. The alphabet of perhaps all languages is faulty, and to devise an entirely new set of hieroglyphs and system of phonetics would no doubt be a fine piece of work—but of doubtful utility. With the new Fedorov and Goldschmidt systems of notation, the old Lévy system still adhered to by French authors, and the various modifications of Schoenflies's notation for the crystal-classes and space-groups, it is becoming increasingly difficult to compare and correlate the work of different authors. And when an author omits to state which system he is using and what are his axes of reference (a matter so obvious to himself) his work is simply useless. The result is chaos, and until some international agreement can be come to little real advance can be expected in crystallography. The logical and concise Millerian system of notation has been systematically adopted in the standard works of Dana, Groth, and Hintz, and will undoubtedly prevail.

A detailed and systematic tabulation of the chief optical constants of minerals has been given by E. S. Larsen.[23] These are put into

[23] "The Microscopic Determination of the Monopaque Minerals," *Bull. U.S. Geol. Survey*, 1921, No. 679.

the form of determinative tables, and so afford a useful means for the identification of non-opaque minerals from such characters as can readily be determined with fragments under the microscope. This method is thus analogous to that of Fedorov mentioned above, but using the optical constants instead of the crystallographic (morphological) constants. One table gives the mean refractive index for a long list of minerals ranging from ice 1·309 to stibnite 4·303. In other tables, the minerals are grouped under the main headings, optically isotropic, uniaxial negative, biaxial positive, etc., the arrangement in each group being according to the value of the refractive index. The tables also state the optical orientation, size of the optic axial angle, density, hardness, and much other useful information. About 950 mineral-species are listed. New data are given for more than 500 species, for many of which no optical data were previously available. Details are given of the useful and rapid method of determining the refractive indices of minute fragments by immersing them in a series of liquids of known refractive index.[24] For ordinary use, methylene iodide sets the limit at 1·74; but this can be raised to 1·87 by dissolving in it sulphur and iodides of tin, arsenic, and antimony. Piperine containing dissolved arsenic and antimony iodides gives at 100° a liquid of refractive index up to 2·10; fusions of sulphur and selenium up to 2·716; and fusions of selenium and arsenic selenide up to 3·17. Tables on the same lines as those of Larsen, but much less extensive, have been compiled by W. H. Fry [25] for a series of inorganic salts.

C. Hintze's well-known and indispensable "Handbuch der Mineralogie," which was commenced in 1889, is still some distance from completion. Since his death in 1916, the work has been carried on under the editorship of G. Linck with the help of various contributors, but not with the same thoroughness and accuracy as it was done by Hintze himself. A number (Lieferung 19) issued in 1921 starts a new pagination for division 4 of volume 1, and commences the borates, aluminates, ferrates, arsenites, and antimonites. Nos. 20 and 21 (1922—1923) carry on with the description of the phosphates, columbates, etc. Vol. 2, dealing with the silicates and titanates, was issued during 1889—1897. C. Doelter's "Handbuch der Mineralchemie," commenced in 1912, has now completed five sectional volumes. The latest part received, No. 9 of Vol. 3, issued in 1922, deals with mercury and commences the "elements of the

[24] A recent modification of the immersion method makes use of the dispersion, the wave-length of light at which there is exact matching being determined with a monochromatic illuminator (H. E. Merwin, *J. Amer. Chem. Soc.*, 1922, **44**, 1970; S. Tsuboi, *Min. Mag.*, 1923, **20**, 108; *A.*, ii, 777).

[25] "Tables for the microscopic identification of inorganic salts," *U.S. Dept. Agric. Bull.*, 1922, No. 1108.

third vertical series," namely, boron, etc. P. Groth and K. Mieleitner's "Mineralogische Tabellen" (München and Berlin, 1921), which is really a new edition in a smaller and handier form of Groth's well-known "Tabellarische Übersicht der Mineralien," gives a systematic classification of minerals with their chemical formula, crystal-class and axial ratios. Attention has already been drawn to the "Tables de Constantes" (p. 273).

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